Chemistry

FOR CLASS XI

PUNJAB TEXTBOOK BOARD, LAHORE

Table 4.2 Periodic table of the elements

Periodic table of the elements

Key: Atomic number — Name — Symbol — Atomic weight — Electron structure (e.g. 11 Sodium **Na** 22.98977, 2 8 1)

*Mass number of most stable or best-known isotope

*Mass of the isotope of longest half-life

Period	Group IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
1	1 Hydrogen **H** 1.0079 (1)																	2 Helium **He** 4.00260 (2)
2	3 Lithium **Li** 6.941 (2 1)	4 Beryllium **Be** 9.01218 (2 2)											5 Boron **B** 10.81 (2 3)	6 Carbon **C** 12.011 (2 4)	7 Nitrogen **N** 14.0067 (2 5)	8 Oxygen **O** 15.9994 (2 6)	9 Fluorine **F** 18.99840 (2 7)	10 Neon **Ne** 20.179 (2 8)
3	11 Sodium **Na** 22.98977 (2 8 1)	12 Magnesium **Mg** 24.305 (2 8 2)	Transition elements										13 Aluminum **Al** 26.98154 (2 8 3)	14 Silicon **Si** 28.086 (2 8 4)	15 Phosphorus **P** 30.97376 (2 8 5)	16 Sulfur **S** 32.06 (2 8 6)	17 Chlorine **Cl** 35.453 (2 8 7)	18 Argon **Ar** 39.948 (2 8 8)
4	19 Potassium **K** 39.098 (2 8 8 1)	20 Calcium **Ca** 40.08 (2 8 8 2)	21 Scandium **Sc** 44.9559 (2 8 9 2)	22 Titanium **Ti** 47.90 (2 8 10 2)	23 Vanadium **V** 50.9414 (2 8 11 2)	24 Chromium **Cr** 51.996 (2 8 13 1)	25 Manganese **Mn** 54.9380 (2 8 13 2)	26 Iron **Fe** 55.847 (2 8 14 2)	27 Cobalt **Co** 58.9332 (2 8 15 2)	28 Nickel **Ni** 58.71 (2 8 16 2)	29 Copper **Cu** 63.546 (2 8 18 1)	30 Zinc **Zn** 65.38 (2 8 18 2)	31 Gallium **Ga** 69.72 (2 8 18 3)	32 Germanium **Ge** 72.59 (2 8 18 4)	33 Arsenic **As** 74.9216 (2 8 18 5)	34 Selenium **Se** 78.96 (2 8 18 6)	35 Bromine **Br** 79.904 (2 8 18 7)	36 Krypton **Kr** 83.80 (2 8 18 8)
5	37 Rubidium **Rb** 85.4678 (2 8 18 8 1)	38 Strontium **Sr** 87.62 (2 8 18 8 2)	39 Yttrium **Y** 88.9059 (2 8 18 9 2)	40 Zirconium **Zr** 91.22 (2 8 18 10 2)	41 Niobium **Nb** 92.9064 (2 8 18 12 1)	42 Molybdenum **Mo** 95.94 (2 8 18 13 1)	43 Technetium **Tc** 98.9062* (2 8 18 14 1)	44 Ruthenium **Ru** 101.07 (2 8 18 15 1)	45 Rhodium **Rh** 102.9055 (2 8 18 16 1)	46 Palladium **Pd** 106.4 (2 8 18 18 0)	47 Silver **Ag** 107.868 (2 8 18 18 1)	48 Cadmium **Cd** 112.40 (2 8 18 18 2)	49 Indium **In** 114.82 (2 8 18 18 3)	50 Tin **Sn** 118.69 (2 8 18 18 4)	51 Antimony **Sb** 121.75 (2 8 18 18 5)	52 Tellurium **Te** 127.60 (2 8 18 18 6)	53 Iodine **I** 126.9045 (2 8 18 18 7)	54 Xenon **Xe** 131.30 (2 8 18 18 8)
6	55 Cesium **Cs** 132.9054 (2 8 18 18 8 1)	56 Barium **Ba** 137.34 (2 8 18 18 8 2)	57 Lanthanum **La*** 138.9055 (2 8 18 18 9 2)	72 Hafnium **Hf** 178.49 (2 8 18 32 10 2)	73 Tantalum **Ta** 180.9479 (2 8 18 32 11 2)	74 Wolfram (Tungsten) **W** 183.85 (2 8 18 32 12 2)	75 Rhenium **Re** 186.2 (2 8 18 32 13 2)	76 Osmium **Os** 190.2 (2 8 18 32 14 2)	77 Iridium **Ir** 192.22 (2 8 18 32 17 0)	78 Platinum **Pt** 195.09 (2 8 18 32 17 1)	79 Gold **Au** 196.9665 (2 8 18 32 18 1)	80 Mercury **Hg** 200.59 (2 8 18 32 18 2)	81 Thallium **Tl** 204.37 (2 8 18 32 18 3)	82 Lead **Pb** 207.2 (2 8 18 32 18 4)	83 Bismuth **Bi** 208.9804 (2 8 18 32 18 5)	84 Polonium **Po** (210)* (2 8 18 32 18 6)	85 Astatine **At** (210)* (2 8 18 32 18 7)	86 Radon **Rn** (222)* (2 8 18 32 18 8)
7	87 Francium **Fr** (223)* (2 8 18 32 18 8 1)	88 Radium **Ra** 226.0254* (2 8 18 32 18 8 2)	89 Actinium **Ac**** (227)* (2 8 18 32 18 9 2)	104 Unnilquadium **Unq** (261)* (2 8 18 32 32 10 2)	105 Unnilpentium **Unp** (262)* (2 8 18 32 32 11 2)	106 Unnilhexium **Unh** (263)* (2 8 18 32 32 12 2)	107 Unnilseptium **Uns** (264)	108 Unniloctium **Uno** (265)	109 Unnilennium **Une** (266)									

Inner transition elements

Series														
* Lanthanide series 6	58 Cerium **Ce** 140.12 (2 8 18 20 8 2)	59 Praseodymium **Pr** 140.9077 (2 8 18 21 8 2)	60 Neodymium **Nd** 144.24 (2 8 18 22 8 2)	61 Promethium **Pm** (145)* (2 8 18 23 8 2)	62 Samarium **Sm** 150.4 (2 8 18 24 8 2)	63 Europium **Eu** 151.96 (2 8 18 25 8 2)	64 Gadolinium **Gd** 157.25 (2 8 18 25 9 2)	65 Terbium **Tb** 158.9254 (2 8 18 27 8 2)	66 Dysprosium **Dy** 162.50 (2 8 18 28 8 2)	67 Holmium **Ho** 164.9304 (2 8 18 29 8 2)	68 Erbium **Er** 167.26 (2 8 18 30 8 2)	69 Thulium **Tm** 168.9342 (2 8 18 31 8 2)	70 Ytterbium **Yb** 173.04 (2 8 18 32 8 2)	71 Lutetium **Lu** 174.97 (2 8 18 32 9 2)
** Actinide series 7	90 Thorium **Th** 232.0381* (2 8 18 32 18 10 2)	91 Protactinium **Pa** 231.0359* (2 8 18 32 20 9 2)	92 Uranium **U** 238.029 (2 8 18 32 21 9 2)	93 Neptunium **Np** 237.0482 (2 8 18 32 22 9 2)	94 Plutonium **Pu** (242)* (2 8 18 32 23 9 2)	95 Americium **Am** (243)* (2 8 18 32 25 8 2)	96 Curium **Cm** (247)* (2 8 18 32 25 9 2)	97 Berkelium **Bk** (249)* (2 8 18 32 26 9 2)	98 Californium **Cf** (251)* (2 8 18 32 27 9 2)	99 Einsteinium **Es** (254)* (2 8 18 32 28 9 2)	100 Fermium **Fm** (253)* (2 8 18 32 29 9 2)	101 Mendelevium **Md** (256)* (2 8 18 32 30 9 2)	102 Nobelium **No** (254)* (2 8 18 32 31 9 2)	103 Lawrencium **Lr** (257)* (2 8 18 32 32 9 2)

CHEMISTRY

FOR

XI CLASS

SHAHZAD BOOK CENTRE

38 - Urdu Bazar, Lahore

FOR

PUNJAB TEXTBOOK BOARD, LAHORE

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PREFACE

This chemistry text book for class XI is based on the revised national curriculum which is being introduced in the country from 1990. It aims at providing a sound base for understanding the basic principles of chemistry. The facts, concepts, principles and methods of chemistry find wide applications in all walks of human life. Chemistry is a unique human enterprise and we believe that it should be accessible to all students who have attained only a general literacy in science. We have, therefore, tried to present the subject in a well organized and readily understandable fashion.

The book is organized into nine chapters. The first chapter is a general introduction to fundamental concepts. Besides presenting an overview of chemistry the aim of this chapter is to develop basic mathematical skills needed for understanding of quantitative relationships in chemistry. Stoichiometry of chemical reactions is introduced right in the beginning to enable the students to handle numerical data with ease and confidence. Mole method is introduced and used throughout the text.

Chemistry is based on the idea that matter is composed of particles such as electrons, protons and neutrons and are organized into atoms, and these atoms further combine to form molecules. These aspects have been elaborated in chapters 4 and 5. Concept of divisibility of atoms is introduced through experiments and periodicity of properties have been discussed with atomic models suggested by wave mechanics in Chapter 4. Chapter 5 includes the modern theories of chemical bonding and enables the students to understand the geometry of simple molecules.

The atoms and molecules are found in various states of organizations as liquids and solids. They also exist in more disordered manner in gaseous state. These three states of matter have been presented in chapters 2 and 3.

Basically chemical reactions represent dynamic modes of changes, and quantitative description of change rests on the

concept of energy. Chapter 6 conveys the concept of first law of thermodynamics and explains that ΔH and ΔE are state functions.

The principles with govern the reversible reactions and quantitative applications of concept of dynamic equilibrium are given in Chapter 7. The discussion of chemical equilibrium is extended for acids, bases and dissociation of salts. Practical applications of acid-base equilibrium involves common ion effect and hydrolysis. These effects help us to understand the buffer solutions and the role of indicators. These discussions are presented in Chapter 8 alongwith phenomenon of oxidation and reduction, which facilitate to follow the formation of electrochemical cells and to balance the chemical equations.

One should be able to measure, control and where possible to predict the rate of chemical reactions. These topics alongwith temperature and effect of catalyst effect on reaction rates are presented in Chapter 9.

We wish to acknowledge our thanks to Riaz Ahmad Khan, Chairman Punjab Textbook Board who has been taking keen interest during all stages of the development of this book and has been providing encouragement and assistance to the editors to complete their work. We are also thankful to Dr. Akbar Hussain (Director Technical) and Mr. Javid Iqbal editor-in-chief for their technical help and support in developing the manuscript. Special thanks are due to Mr. M. Munawar Javid an author and the sub-editor who kept a liaison between authors, editors and local members of the National Review Committee, Ch. Sana Ullah and Dr. B.A. Nasir and also watched the progress of printing work upto the last moment.

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1

INTRODUCTION TO FUNDAMENTAL CONCEPTS

1.1 What is Chemistry?

The word chemistry has actually taken its origin from the Arabic term "Alkimiya" which later became alchemy, a knowledge developed by ancient Egyptians and Arabs during the middle ages to convert baser metals into gold. However, many Muslim alchemists were not interested in preparing gold. They developed the knowledge and techniques of chemistry to study properties and interconversions of materials occurring in nature and to prepare medicines for curing various diseases. By the thirteenth century alchemy had spread to Europe, primarily as a result of contacts between the crusaders and the Arabs. As time went on, alchemy changed from a semi-scientific practice, filled

with mystical concepts, into the science of chemistry with which we are familiar today.

Now, chemistry is concerned with the study of the composition, structure, properties, changes in matter, changes in energy. It also deals with laws and principles which govern these changes.

Presently the well known branches of this discipline of knowledge are: Physical Chemistry, Inorganic Chemistry, Biochemistry, Nuclear Chemistry, Analytical Chemistry and Industrial Chemistry.

1.2 Element and Molecule

According to modern concept all ordinary matter is composed of extremely tiny entities called atoms. These atoms, though being the building blocks of matter, consist of still smaller particles, the most important of which, for the chemists are (i) protons, (ii) neutrons and (iii) electrons. The idea that matter is atomic in nature, is the most important concept developed by chemists which provided a basis of a revolution in the quest of knowledge.

A sample of pure matter is often called a substance. If all the atoms in a substance are chemically identical, the material is called an *element.* Pure iron, for example, is an elemental substance because it consists of solely iron atoms. Currently 110 different elements are known. These atoms, either individually or in various combinations, compose all known kinds of matter. If a substance of definite composition by weight consists of atoms of two or more different elements, it is called a *compound.* Water, for example, is a compound because it consists of hydrogen and oxygen atoms in a definite, fixed proportion.

1.3 Physical and Chemical Properties

The *Physical properties* of any element or a compound

are those characteristics which serve to distinguish it from other substances but which do not deal with its ability to undergo chemical changes. Example of physical properties are *melting point, boiling point, solubility* and *density*. When ice melts, a *physical change* takes place. Notable is the fact that both ice and water have the same chemical composition and the same chemical properties. They are merely different *physical forms* or physical states of the same substance.

c/ *Chemical properties* indicate the ability of a substance to undergo chemical changes. Chemical changes always involve the making or breaking of *chemical bonds*, resulting in the formation of new substances. The burning of a piece of paper represents a chemical change. In this process the cellulose of paper reacts with oxygen of air to produce CO_2 and H_2O which are different in all respects from cellulose and O_2.

1.4 Units of Measurement

In dealing with the properties of substances, scientists the world over make use of an international system of units of measurements. These units are known as the SI units after the *"French words System Internationale"*.

The basic SI unit commonly used in chemistry are metre for length, kilogram for mass, second for time, ampere for electric current, Kelvin for thermodymanic temperature and mole for the amount of substance.

1.4.1 Metre

The standard unit of length in SI units is the *metre*. It is the distance light travels in a *vacuum* in 1/299,792,458 seconds. The fractions and multiples of metre are shown in table 1.1.

Table 1.1 SI Units of Length

Unit		Abbreviation	Metre equivalent
1. tera metre	T	Tm	10^{+12}
2. giga metre	G	Gm	10^{+9}
3. megametre	M	Mm	10^{+6}
4. kilometre	k	km	10^{3}
5. hectometre	h	hm	10^{2}
6. decametre	da	dam	10
7. metre	-	m	1
8. decimetre	d	dm	10^{-1}
9. centimetre	c	cm	10^{-2}
10. millimetre	m	mm	10^{-3}
11. micrometre	μ	μm	10^{-6}
12. nanometre	n	nm	10^{-9}
13. pico metre	p	pm	10^{-12}
14. femto metre	f	fm	10^{-15}
15. attometre	a	am	10^{-18}

1.4.2 Volume

The SI unit for the volume is cubic metre (m^3). Chemists, however, usually use a smaller unit i.e., a cubic decimetre (dm^3)

Since $1\ dm = 10^{-1}\ m$

So, $1\ dm^3 = 10^{-3}\ m^3$

or $1\ dm^3 = \frac{1}{1000}\ m^3$

Similarly

$1\ cm = 10^{-2}\ m$

$1\ cm^3 = 10^{-6}\ m^3$

or $1\ cm^3 = \frac{1}{10^6}\ m^3$

$1\ dm^3$ is also called one litre (L). One litre is equal to the volume occupied by one kilogram by weight of pure water at 4°C (39.2°F). Other commonly used volume units are the *millilitre* (mL.), equal to 0.001 litres and the cubic centimetre (cm^3), which is the same as the millilitre.

1.4.3 Mass

The SI unit for *mass* is the kilogram (equivalent to 2.2046 lb) and abbreviated as kg, the *gram* (g), equal to 0.001 kg and the *milligram (mg)*, equivalent to 0.001g. The standard kilogram is a cylinder of platinum-iridium alloy kept at the Bureau of Weights and Measures in Sevres.

1 kg = 1000g

or

1 g = 0.001 kg

and

1 g = 1000 mg

or

1 mg = 0.001 g

1.4.4 Mass and Weight

A distinction must be made between *mass* and *weight*. The *mass* of an object is directly related to the amount of matter which it contains, and is a measure of its inertia. *Mass* of an object remains constant regardless of where the object may be located in the universe. *Weight*, on the other hand, pertains to the force which the *earth's gravity* exerts upon the object. It changes with the change in the distance of an object from the earth's centre. In outer space, the object is weightless but it still possesses mass. At any given point on the earth's surface, however, the weights of two different objects are directly proportional to their masses. Hence there is a tendency to use the two terms interchangeably, in this text as well as elsewhere.

1.4.5 Atomic Mass and Atomic Mass unit

An important number which is used to describe an element is the atomic mass, formally called atomic weight. Measurement of atomic weights began with John Dalton. Dalton had no way of measuring the weight or masses of individual atoms. He devised method of measuring the relative weights of atoms i.e. the weight of one atom compared with that of any other.

Mass is more fundamental unit than weight and modern physical methods are more accurate than older chemical methods of determing atomic weights, so the term atomic mass is prefered over atomic weight. Anyhow, we will use both terms interchangeably.

Hydrogen atom is no longer used as the standard for measuring atomic masses. The modern standard is a particular type of carbon whose mass is exactly 12.0000 units. The carbon is chosen as standard because it is a stable and enters into many compounds, and the relative masses of other elements can be measured conveniently. The standard carbon is called carbon-12 (Naturally occuring carbon has atomic mass of 12.011 units). The atomic mass unit is defined as 1/12 the mass of a carbon-12 and is abbreviated as a.m.u. Its value is 1.6×10^{-28} g.

1.4.6 Temperature

There are three measuring scales for temperature;

(*i*)	Fahrenheit scale	(°F)
(*ii*)	Centrigrade scale	(°C)
(*iii*)	Kelvin scale	(K)

(consult chapter 2 for details).

The interconversion formulas for various scales of temperatures are;

$$C^{\circ} = \frac{5}{9}(F\text{-}32)$$

or

$$\text{Kelvin} = 273.16 + {}^\circ\text{C}$$

or

$$\text{K} \approx 273 + {}^\circ\text{C}$$

1.4.7 Energy

Heat, a form of energy , is also measured in SI units. The SI unit of heat, or any other form of energy is joule (J). It is defined as the energy expended when a force of one newton moves an object one metre in the direction in which the force is applied.

$$1\ \text{J} = 1\ \text{N m}$$

$$1\ \text{N} = 1\ \text{Kgs}^{-2}$$

Therefore, $$1\ \text{J} = \text{Kg}^2\text{s}^{-2}$$

The unit of heat is the calorie (cal.). One calorie is defined as the quantity of heat required to raise the temperature of one gram of water from 14.5 °C to 15.5 °C.(1 cal = 4.1868 J).

Units of some important physical parameters, as of viscosity, surface tension, vapour pressure, dipole moment and rate constant of a reaction are mentioned in respective chapters (also see appendix).

1.4.8 Matter and Energy

The most common forms of energy are; heat, electromagnetic radiations, electric, kinetic, potential and mechanical energies.

Albert Einstein in 1905 proposed his classic theory that matter and energy are equivalent. A simple relationship that expresses this equivalence is $E = mc^2$. According to this expression, the conversion of one gram of matter to energy yields 9×10^{16} J. This amount of heat could raise the temperature of 2.5×10^8 Kg of water from 0 °C to 100 °C.

It should be recognised that the amount of this energy available in a given sample of matter is dependent only on the mass of the matter and not on the character of the matter itself.

The amount of energy evolved during an ordinary chemical reaction is extremely small in contrast to the total mass of matter involved in the chemical change. For instance, during the combustion of 3×10^6 Kg of coal only 1 g of matter is converted to energy. This means that the loss of mass per gram of coal is 0.33×10^{-9}g. Since this minute difference in mass cannot be detected by routine procedures, the loss in mass during the burning process is usually ignored. Also we have learnt that atomic nuclei do not undergo changes during ordinary chemical reactions.

1.5 Exponential Notation

A chemist usually encounters very small and very large numbers while working with his problems. Such numbers are not only difficult for him to write but the chance of making an error while dealing with them is also great. For example recording correct number of zero of Avogardro's number as 602,200,000,000,000,000,000,000, or Planck's constant as 0.000,000,000,000,000,000,000,000,000,000,00,066262 Js, or the mass of an individual hydrogen atom as 0.000,000,000,000,000, 000,000,167 g., would be a tedious work. This situation is avoided by writing the numbers in exponential form called exponential notation. Take for example the number 100. This is equal to $10 \times 10 = 10^2$. Similarly 1,000,000 is $10 \times 10 \times 10 \times 10 \times 10 \times 10$ or 10^6. In these two examples the exponent of 10 is equal to the number of zeros following the first digit of the number. And this is a short way of expressing a large number of zeros. Consider the following series.

$$1 = 10^0$$

$$10 = 10^1$$

$$100 = 10^2$$

$$10{,}000 = 10^4$$

$$1{,}000{,}000 = 10^6$$

$$10{,}000{,}000{,}000{,}000 = 10^{13}$$

Now suppose that we have the number 70345. This quantity is the same as 7.0345 x 10,000 and since 10,000 = 10^4, the number can be written as 7.0345 x 10^4. Take the case of Avogardro's number which can be written as

6.022 x 100,000,000,000,000,000,000,000

or in exponential form as 6.022 x 10^{23}.

Let us see how to deal with very small numbers by converting them to the exponential form. The number 0.01, for example, is equal to 1/100 or 1/10^2. And as it is known that dividing by a number 10^2 is same as multiplying by 10^{-2} and hence 0.01 = 10^{-2}. Thus

$$0.1 = 10^{-1}$$

$$0.01 = 10^{-2}$$

$$0.001 = 10^{-3}$$

$$0.0001 = 10^{-4}$$

$$0.00001 = 10^{-5}$$

$$0.0000000001 = 10^{-10}$$

As we observe from the above digits, if there are no zeros between the decimal point and the first digit of the number, the exponent is −1 and if there is one zero between the decimal and the first digit the exponent is −2; if two zeros the exponent is −3 and so on. Thus the Planck's constant which carries 33 zeros between the decimal point and the first digit can be written exponentally as 6.626 x 10^{-34} Js.

1.5.1 Calculation with Exponential Notation

Multiplication

While multiplying the exponentially expressed numbers, their exponents are added up.

Thus:(i) $0.022 \times 0.004 \times 750 = (2.20 \times 10^{-2})\ (4.0 \times 10^{-3})(7.5 \times 10^{2})$
$= 6.6 \times 10^{-2}$

(ii) $(5 \times 10^{6})(7 \times 10^{9}) = 35 \times 10^{15} = 3.5 \times 10^{16}$

(iii) $(6 \times 10^{20})(0.5 \times 10^{-12}) = 3.0 \times 10^{8}$

Division:

Similarly while dividing the exponential numbers, the exponents are substracted:

(i) $$\frac{9.0 \times 10^{19}}{3.0 \times 10^{9}} = 3.0 \times 10^{19-9} = 3.0 \times 10^{10}$$

(ii) $$\frac{3.0 \times 10^{-8}}{9.0 \times 10^{-19}} = 0.33 \times 10^{19-8} = 0.33 \times 10^{11} = 3.3 \times 10^{10}$$

(iii) $$\frac{20 \times 636 \times 0.15}{0.0400 \times 1.80} = \frac{(2 \times 10)(6.36 \times 10^{2})(1.50 \times 10^{-1})}{4.00 \times 10^{-2} \times 1.80}$$

$$= \frac{2 \times 6.36 \times 1.5 \times 10^{1+2-1}}{4 \times 1.80 \times 10^{-2}}$$

$$= \frac{19.08 \times 10^{2}}{7.2 \times 10^{-2}}$$

$$= 2.65 \times 10^{4}$$

It is a custom in exponential expression to multiply some power of ten with a number between 1 and 10. Therefore rather than writing 36×10^{10} for example, we generally write 3.6×10^{11} ($= 3.6 \times 10^{1} \times 10^{10}$) and instead of writing 0.075×10^{-7}, we write 7.5×10^{-9} ($= 7.5 \times 10^{-2} \times 10^{-7}$).

When an exponential number is itself raised to some power, the exponent is multiplied by the power to which the number is being raised, e.g.,

$$(2.7 \times 10^{-6})^{2} = (2.7)^{2}(10^{-6})^{2} = 7.29 \times 10^{-12}$$

$$(5.0 \times 10^{5})^{3} = (5)^{3}(10^{5})^{3} = 125 \times 10^{15} = 1.25 \times 10^{17}$$

$$(9.0 \times 10^{8})^{1/2} = (9)^{1/2}(10^{8})^{1/2} = 3 \times 10^{4}$$

Raising a number to the 1/2 power is similar to taking a square root of that number as shown in the last expression above; that is why if the square root of an exponential number is to be taken, it is best to express the number in such a way that the exponent is divisible by two. Thus

$$(28.9 \times 10^3)^{1/2} = (289 \times 10^2)^{1/2} = 17 \times 10^1 = 170$$

Similarly if the cube root of a number is required, the exponent should be divided by 3 and so on.

$$(36.4 \times 10^8)^{1/3} = (3.64 \times 10^9)^{1/3} = 1.538 \times 10^3 = 1538$$

1.6 Significant Figures

The concept of significant figures is directly related to the accuracy of measurements that are made in scientific work. It should be explicitly understood because we can understand the precision of a measurement if we have the knowledge of its significant numbers. Let us suppose, for example, that an object is being weighed on two different types of balances, one a relatively crude balance and the other a very sensitive analytical balance with higher degree of accuracy.

The results are:

	Rough Balance	Analytical Balance
Measured Quantity	10.3g	10.3106g
Uncertainty	±0.1g	±0.0001g
Mass (Weight)	10.3±0.1g	10.3106±0.0001g
Precision	Low	High

These figures clearly show that the weighing on rough balance is reproducible to the nearest 1/10th gram ± 0.1g whereas on the analytical balance the measurement is reproducible to the nearest 1/10th milligram (±0.0001g). The notations 10.3 ±0.1g and 10.3106 ±0.0001g indicate the precision of these measurements very clearly. Although it is the usual notation employed in scientific journals, it is however cumbersome, in writing.

An alternate approach is to assume that all the digits in a number showing the measurement except the last digit are known with certainty and there is an uncertainty of about one unit in the last digit shown. Thus the number 10.3 stands between 10.2 and 10.4, whereas the number 10.3106 is between 10.3105 and 10.3107. The number 10.3 is said to consist of three significant figures whereas 10.3106 consists of six significant figures. This means that showing the number of significant figures in a quantity is to indicate the confidence with which a number can be known. Greater the number of significant figures in a quantity, greater the certainty and precision in that quantity and smaller the uncertainty.

As a rule when zeros are used merely to locate a decimal point they are not significant. For example, the numbers 0.034, 0.0034, 0.00034 each have only two significant figures. But when zeros appear between the digits of a number, they are significant. For example the number of significant figures in 1.002, 12.003, 10.0009 are 4,5 and 6 respectively. Zeros are also significant if they follow a decimal point and conclude a number. For example, the measurement 45.600 has five significant figures.

1.7 Rounding off Data

We must learn how to round off the numbers used in expressing a quantity. The rule to follow in "rounding off" is to drop the last digit and to increase the final remaining digit by one unit if the digit dropped is greater than 5 and to leave the final remaining digit unchanged if the digit dropped is less than 5. For example, to get three significant figures, 15.56 rounds off to 15.6 and 15.54 rounds off to 15.5. But if the digit dropped is 5, the final remaining digit is increased by one unit if it is odd and left unchanged if it is even. Thus for three significant figures, 25.55 is rounded off to 25.6 and 75.45 is rounded off to 75.4.

One should apply the concept of significant figures where it is seriously needed in the solution of a numerical problem. On the other hand one should use the common sense

in situations where substantial errors can occur by the strict application of the rule. The example of multiplication of 0.1395 by 2 illustrates this aspect of the application of significant figures. The use of rounding off figures can be illustrated from the following example.

Suppose the density of a metallic rectangular block is to be determined. Its dimensions are: length 5.3 cm., width 2.6 cm, height 1.2 cm. In recording the dimensions in this way we imply that value of each figure is known to the nearest 0.1 cm. In other words when we say that the length is 5.3 cm, we mean that it is no less than 5.25 cm and no more than 5.35 cm. The second figure in each measurement is, therefore, significant, although somewhat uncertain. By multiplying length x width x height, we get the volume to be 16.536 cm^3. But to record this value in the figures would mean that we know it to the nearest figure of 0.001 cm^3 which is not true, since the measurements of length and width etc. are known only by the nearest figure of 0.1 cm. For this reason we round off the volume to 17 cm^3, a number with two significant figures, the same as in original measurements.

Now, for example, using an analytical balance we find that the block weighs 44.8963g. Dividing this weight by the volume gives us the density.

$$\text{Density} = \frac{44.8963\text{g}}{17\ \text{cm}^3} = 2.6409\text{g/cm}^3$$

Once more our answer is more precise than what actually it should be. Although the mass of the block is known to six significant figures, its volume is known only to two significant figures. And we know that the result of a division or multiplication cannot be more precise (cannot have more significant figures) than the least precise item of the data used in the calculation. Therefore, the result obtained in this problem should be rounded off to 2.6g/cm^3 two significant figures — the same as the volume which is the least precise figure in this case.

1.8 Precision and Accuracy-Concept of Error

Precision and accuracy are two important but quite different terms in chemical calculations. The precision of a series of experiments is determined by the fact that how closely the measurements agree with one another. While accuracy is determined by the fact that how closely the results agree with the accepted value. It is the fundamental job of a scientist to strive for the both, but it is quite possible for his work to be precise without being accurate or accurate without being precise. In order to see this difference in actual practice, let us take an example. Two students are given the same sample of K_2CO_3 for analysis which we know to contain 45.6% of K_2CO_3. The students are required to report the average of three separate analysis. One student is working very carefully, but his burette being not accurately calibrated, obtains the following results.

No. of Analysis	% of K_2CO_3
1	46.92
2	46.91
3	46.93
	46.92 ± 0.01

It may be noted that the work done by the student is precise as shown by the close agreement amongst the three experimental measurements. But at the same time the result is not particularly accurate. The error being 46.92 − 45.6 = 1.32 parts in 45.6, or nearly 2.9%. This shows that the work of the student is precise but not accurate on account of faulty apparatus.

It is noted about the second student that he is comparatively careless in his work but obtains the following results.

No. of Analysis	% of K_2CO_3
1	45.3
2	44.6
3	47.1
Average	45.66 ± 1.01

In this case the work is not precise. But by a lucky accident, the average of the three analyses differs from the correct value by only a very small amount i.e., 0.06, or 0.13%. We should not, however feel encouraged from this example that careless work leads to accurate results. But the fact is that a careful work is more likely to be accurate as well as precise.

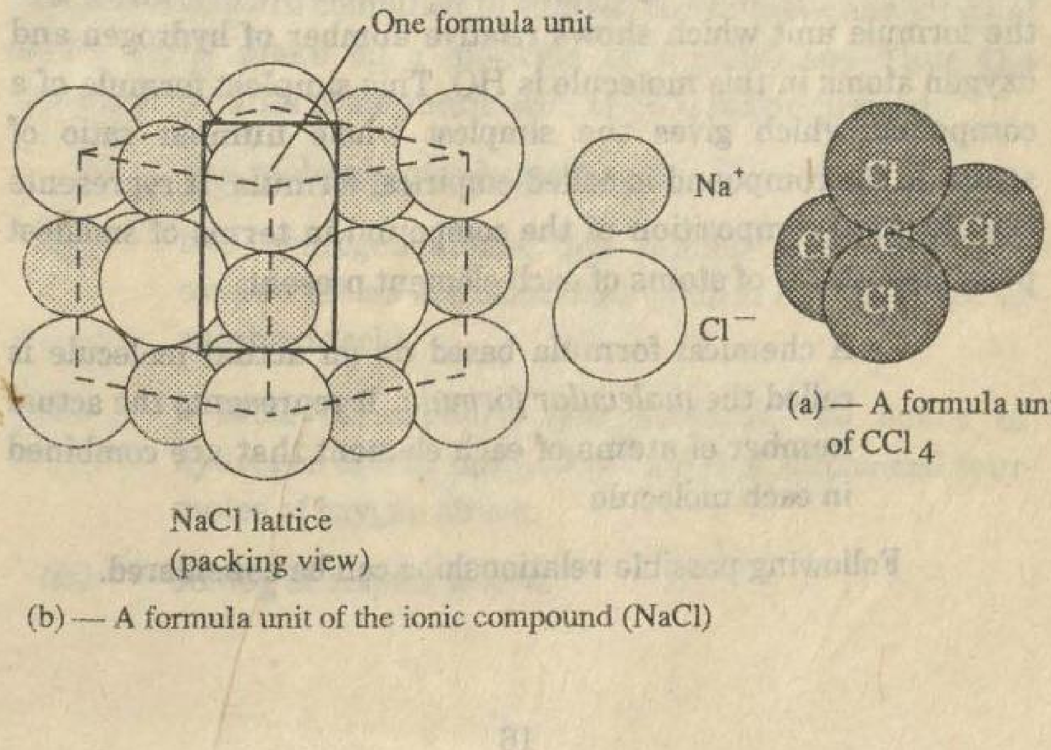
1.9 Chemical Compounds and Their Formulas

Chemical compounds are pure substances composed of two or more elements and are represented by combination of symbols known as chemical formula. To establish the formula of a compound, it is essential to determine a formula unit. A formula unit is the smallest collection of atoms which tells us that:

(i) What types of atoms are present in the compound.

(ii) The relative number of atoms of each type present in the compound.

For example the formula of water (H_2O) indicates the actual number of atoms in one unit formula of the substance. The formula H_2O indicates that two atoms of hydrogen and one atom of oxygen constitute the molecule of water.



NaCl lattice (packing view)

(b) — A formula unit of the ionic compound (NaCl)

(a) — A formula unit of CCl_4

Here are some additional formula units.

$NaCl$, K_2SO_4, CCl_4, C_2H_6, H_2O_2

But these formulas units do not give us much information about the structure of substances. For example an important distinction between a formula unit of NaCl and the formula unit of CCl_4 is suggested in Fig. 1.1.

As illustrated in the figure 1.1 (a) formula unit of CCl_4 exists as a separate unit or entity hence each entity represents one molecule. **A combination of a certain number of atoms that can exist independently as a separate distinguishable unit is called a molecule.** Hence formula unit and molecule of carbon tetrachloride are identical. But a formula unit of NaCl is simply a pair of ions which can be a basic unit of huge arrangements of ions Fig. 1.1 (b). So it shall be inappropriate to call NaCl as a molecule. NaCl is the formula unit. All ionic compounds like NaCl, K_2SO_4, $MgCl_2$ etc. have the formula units which do not represent a molecule of these substances.

1.10 Empirical and Molecular Formula

Let us consider another situation with the compound hydrogen peroxide(H_2O_2). The molecule of hydrogen peroxide contains two atoms of hydrogen and two atoms of oxygen. But the formula unit which shows relative number of hydrogen and oxygen atoms in this molecule is HO. This simplest formula of a compound which gives the simplest whole number ratio of atoms in the compound is called empirical formula. It represents the chemical composition of the compound in terms of smallest possible number of atoms of each element present.

A chemical formula based on an actual molecule is called the *molecular formula.* It represents the actual number of atoms of each element that are combined in each molecule.

Following possible relationships can be considered.

(i) The empirical and molecular formula may be identical as in case of CCl_4, H_2O, SO_2 etc.

(ii) The molecular formula may also be a multiple of the empirical formula. In case of the compound hydrogen peroxide, H_2O_2 is twice the empirical formula (HO). Or in case of benzene, the molecular formula C_6H_6 is six times the empirical formula (CH). This relationship can be expressed as

Molecular Formula = n x empirical formula

where 'n' is an integer, and it shows the ratio of molecular weight and empirical formula weight.

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

(iii) A compound may have an empirical formula such as NaCl, K_2SO_4 etc. and no molecular formula. The reason is that no independent molecule of NaCl etc, exists in the crystal structure of NaCl.

1.11 Chemical Formulas and Chemical Analysis

A compound is represented by a chemical formula in which symbols are combined to express the number and kinds of atoms which make up a molecule of a substance. Thus the molecular formula of sulphuric acid, H_2SO_4 may represent:

(i) one molecule of sulphuric acid

(ii) two hydrogen atoms, one sulphur atom and four oxygen atoms are combined to form one molecule of sulphuric acid.

(iii) a mole of sulphuric acid contains two moles of hydrogen atoms, one mole of sulphur atoms and four moles of oxygen atoms.

(iv) 98.08g of sulphuric acid.

But to determine the formula of a compound it is necessary to perform a chemical analysis. Chemical analysis is an experimental procedure by which the different amounts of various elements present in the compound are determined. One method of analysis used for a large variety of organic compounds is combustion analysis. A weighed quantity of the compound is burned in a closed tube in a stream of oxygen. The hydrogen and carbon contained in the compound are converted to H_2O and CO_2 gas respectively. The CuO placed at the end of combustion tube ensures complete combustion. The water vapour is absorbed in a substance like magnesium perchlorate and carbon dioxide in potassium hydroxide solution. The increase in weight of these absorbers corresponds to the masses of water and

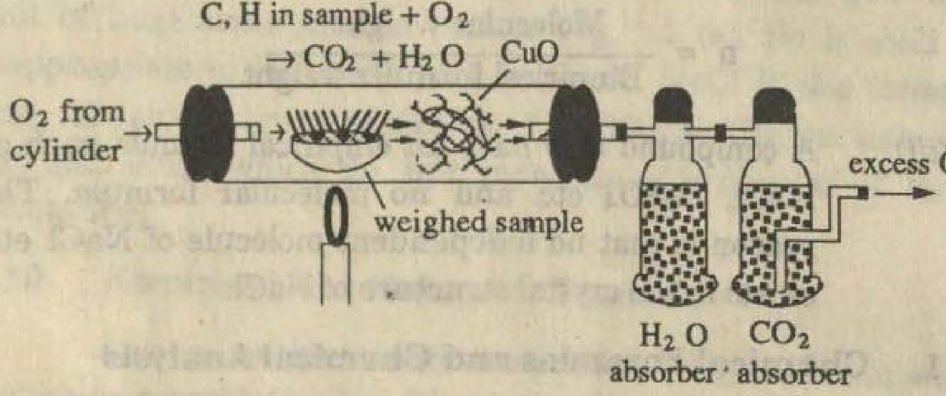


Fig. 1.2 — Experimental determination of the percentages of C and H in a compound

carbon dioxide produced in the combustion of the organic compound. From these increases the percentages by weights of these elements can be calculated. Other absorbers can be used for other products of the combustion. The formulas for percentage of carbon and hydrogen are,

$$\% \text{ of Carbon} = \frac{\text{Weight of } CO_2}{\text{Weight of organic compound}} \times \frac{12}{44} \times 100$$

$$\% \text{ of Hydrogen} = \frac{\text{Weight of } H_2O}{\text{Weight of organic compound}} \times \frac{2}{18} \times 100$$

$$\% \text{ of Oxygen} = 100 - (\% \text{ of Carbon} + \% \text{ of Hydrogen})$$

1.11.1 Percentage Composition and Determination of Empirical Formula

Each symbol in the formula of a compound represents among other things, the mass of one mole of atoms of the element. The formula represents the mass of one mole of the compound. From this information, the percentage composition by mass of the compound can be calculated by using the formula

$$\% \text{ of an element} = \frac{\text{At. weight of element}}{\text{Molecular weight}} \times 100$$

Following steps are carried out to determine empirical formula of a compound.

(i) Divide the % of each element by atomic weight of element to get mole ratios.

(ii) Divide the mole ratios by smallest figure to get atomic ratios.

(iii) If the resulting values are simple whole numbers well and good, otherwise multiply with a small suitable figure to get so.

Example 1

Calculate the percentage composition of each element in anhydrous copper sulphate, $CuSO_4$.

Solution

The formula indicates that there is one mole of copper, one mole of sulphur and four moles of oxygen atoms in one mole of copper sulphate. Converting these molar quantities into their respective masses gives 63.54g of Cu, 32.06g of S and 4 x 16.00 = 64.00g of O and 63.54 + 32.06 + 64.00 = 159.60g of $CuSO_4$. The percentage of each element in the compound is then:

$$\% \text{ Cu} = \frac{63.54\text{g}}{159.60\text{g}} \times \frac{100}{1} = 39.81\%$$

$$\% S = \frac{32.06g}{159.60g} \times \frac{100}{1} = 20.09\%$$

$$\% O = \frac{64.00g}{159.60g} \times \frac{100}{1} = 40.10\%$$

Example 2

0.206g of an organic compound (O.C) containing carbon, hydrogen and oxygen was subjected to combustion analysis. The amounts of CO_2 and H_2O produced are 0.494g and 0.1011g respectively. Determine the percentage composition of the compound.

Solution

Weight of organic compound = 0.206 g

Weight of carbon dioxide = 0.494 g

Weight of water = 0.1011 g

$$\% \text{ of carbon} = \frac{0.494g \text{ of } CO_2}{0.206g \text{ of O.C.}} \times \frac{12}{44} \times 100 = 65.44$$

$$\% \text{ of Hydrogen} = \frac{0.1011g \text{ of } H_2O}{0.206 \text{ g of O.C.}} \times \frac{2}{18} \times 100 = 6.72$$

$$\% \text{ of Oxygen} = 100 - (65.44 + 6.72) = 53.29$$

Example 3

Grape sugar, or glucose, contains only carbon, hydrogen and oxygen. Combustion of a sample of 0.1802g of glucose yields 0.2641g of CO_2 and 0.1081g of H_2O. Calculate the percentage of each element in the compound. Also calculate the simplest formula of glucose.

In another experiment the molecular weight of glucose was determined as 180.18g/mol. Find out the molecular formula of the compound.

Solution

$$\% \text{ of carbon} = \frac{0.2641\text{g } CO_2}{0.1802\text{g glucose}} \times \frac{12.01\text{g C}}{44.01\text{g } CO_2} \times \frac{100}{1} = 39.99\%$$

$$\% \text{ of Hydrogen} = \frac{0.1081\text{g } H_2O}{0.1802\text{g glucose}} \times \frac{2.02\text{g H}}{18.02\text{g } H_2O} \times \frac{100}{1} = 6.72\%$$

$$\% \text{ of oxygen} = 100 - (39.99 + 6.72) = 53.29\%$$

Now percentage compositions of all the elements present in glucose can be converted into the respective mole ratios as under

$$\frac{39.99\text{g carbon}}{12.01\text{g/mol carbon}} = 3.33 \text{ moles of carbon}$$

$$\frac{6.72\text{g hydrogen}}{1.01\text{g/mol hydrogen}} = 6.65 \text{ moles of hydrogen}$$

$$\frac{53.29\text{g}}{16.00\text{g/mol}} = 3.33 \text{ moles of oxygen}$$

The atomic ratios of various elements present in glucose are therefore, 3.33:6.65:3.33. Now we bring these ratios to the nearest whole number by dividing these ratios by the smallest quotient.

$$\text{C} : \text{H} : \text{O}$$

$$\frac{3.33}{3.33} : \frac{6.65}{3.33} : \frac{3.33}{3.33} \quad \text{or } 1 : 2 : 1$$

The simplest formula expressing this ratio in glucose is CH_2O. In order to calculate the molecular formula we divide molecular weight by simplest formula weight i.e. 30, to get n.

$$\therefore \quad n = \frac{180.18}{30} = 6$$

So, Mol. Wt. = 6 $[CH_2O]$ = 6[12+2+16] = 6 x 30 = 180

This means that molecular formula of glucose is 6 times the simplest (empirical) formula. The molecular fo mula of glucose thus becomes 6(CH_2O); i.e. $C_6H_{12}O_6$.

Example 4

A compound contains 65.44% C, 5.49% H and 29.07% O. What is its empirical formula. If molecular weight of the compound is 110, calcualte the molecular formula.

Solution

$$\text{No. of moles of C} = \frac{65.44 \text{ g of C}}{12.01 \text{ g/mol of C}} = 5.45 \text{ moles}$$

$$\text{No. of moles of H} = \frac{5.49 \text{ g of H}}{1.01 \text{ g/mol of H}} = 5.44 \text{ moles}$$

$$\text{No. of moles of O} = \frac{29.07 \text{ g of O}}{16.00 \text{ g/mol of O}} = 1.82 \text{ moles}$$

The relative number of moles of different elements in the compound, therefore, are;

C	:	H	:	O
5.45	:	5.44	:	1.82

But formula units contain integral (whole) numbers of atoms. For this reason we divide all mole ratio values by the smallest quotient.

	C	:	H	:	O
	$\frac{5.45}{1.82}$	:	$\frac{5.44}{1.82}$	:	$\frac{1.82}{1.82}$
or	2.99	:	2.99	:	1
or	3	:	3	:	1

(by rounding off small fractions)

Thus empirical formula can be written as C_3H_3O.

Now empirical formula weight = (12.01x3 + 1.01x3 + 16.00) = 55.06. Since the molecular formula weight is almost exactly twice the empirical formula weight (110/55 = 2), the molecular formula is twice the empirical formula i.e. $2(C_3H_3O) = (C_6H_6O_2)$.

1.12 Avogadro's Number and the Concept of the Mole

While studying weight relationships in chemical reactions we weigh the substances in a balance in grams. But when we carry out the reactions we know that the reactions occur between atoms, molecules and ions. For example, the reaction between magnesium and sulphur is represented as under:

$$Mg + S \longrightarrow MgS$$

It indicates that one atom of magnesium reacts with one atom of sulphur. When we measure the masses of these two elements we find that 24.3g of Mg reacts with 32.06g of S. Because Mg and S react in 1:1 atomic ratios we can conclude that 24.3g of Mg contain the same number of atoms as are present in 32.06g of S. How many atoms are in 24.3g Mg or 32.06g S? The two amounts contains one mole of atoms each.

The mole is one of the basic unit, in the International System (SI) of measurements. It is a counting unit like a dozen or a gross. Mole, however, is a very large counting unit. It is equal to 6.022×10^{23} things, atoms, molecules, ions or electrons, things, a chemist deals with. The number 6.022×10^{23} is known as Avogadro's number (abbreviated as N). A mole is a quantity containing Avogadro's number of units (atoms, molecules, ions or whatever) under consideration. Thus, we may write:

Avogadro's number is the number of atoms, molecules or ions in one gram atom, one gram mole or one gram ion of a substance, respectively. Its value is 6.02×10^{23}. Hence one mole of a substance contains 6.02×10^{23} particles.

This number is an excellent tool to correlate the numbers and weights of atoms, molecules and ions in elements and compounds.

For examples,

1 mole of ${}_6C^{12}$ consists of 6.022×10^{23} atom of carbon and weighs 12.00g

1 mole of ${}_8O^{16}$ consists of 6.022×10^{23} atom of oxygen and weighs 15.9994g

1 mole of water consists of 6.022×10^{23} molecules of water and weighs 18.00 g.

1 mole of OH^- ions consists of 6.022×10^{23} ions of hydroxyl group and weighs 17.00 g.

Quantities are generally more meaningful to a chemist if expressed in moles rather than in grams because it makes calculations simple and exact. For example, a chemist wishing to prepare a compound in which he knows there are two atoms of sodium for every atom of sulphur, actually, he needs two moles of sodium atoms for every mole of sulphur atoms. The application of mole concept in chemical calculations is illustrated by the following examples.

Example 5

How many moles and atoms of sulphur in 15.0g of the element?

Solution

The atomic weight of sulphur is 32.1 a.m.u., therefore weight of one mole is 32.1g.

$$\text{Moles of sulphur} = \frac{\text{Wt.of sulphur}}{\text{At. wt of S}} = \frac{15.0\text{g}}{32.1\text{g}} = 0.467\text{moles}$$

$$\text{No. of atom of S} = \text{No. of moles} \times 6.022 \times 10^{23}$$

$$= 0.467 \times 6.022 \times 10^{23}$$

$$= 2.18 \times 10^{23}$$

Example 6

How many moles of Mg are represented by a collection of 3.05×10^{20} atoms of Mg.

Solution

Again the definition of mole is helpful.

1 mole of Mg = 6.022×10^{23} atoms of Mg.

$$\text{No. of moles of Mg} = \frac{\text{Atoms of Mg}}{\text{No. of atoms in 1 mole of Mg}}$$

$$= \frac{3.05 \times 10^{20}}{6.022 \times 10^{23}} = 0.5064 \times 10^{-3}$$

$$= 5.064 \times 10^{-4}$$

Example 7

How many individual calcium atoms are there in 20g of the metal?

Solution

We shall use two relationships for the solution of this problem.

(i) conversion from grams to moles and *(ii)* conversion from moles to atoms.

$$\text{No. of moles of Ca} = \frac{\text{Wt. of Ca}}{\text{At. Wt. of Ca}}$$

$$= \frac{20.00}{40.00} = 0.5$$

$$\text{No. of atoms of Ca} = \text{No. of moles} \times 6.022 \times 10^{23}$$

$$= 0.50 \times 6.02 \times 10^{23}$$

$$= 3.01 \times 10^{23}$$

Example 8

What is the mass, in kilograms, of a collection of 5.60×10^{25} atoms of copper?

Solution

$$\text{No of moles of Cu} = \frac{5.60 \times 10^{25}\ \text{atoms of Cu}}{6.022 \times 10^{23}\ \text{atoms/mol}} = 92.99$$

But 1 mole of Cu = 63.54g of Cu

or

= 0.06354 kg of Cu

Thus mass of Cu = 92.99 moles x 0.06354 moles/kg

= 5.91 kg

1.13 Calculations Based on Chemical Equations (Stoichiometry)

Stoichiometry is the branch of chemistry which deals with the study of relationship between the quantities of reactants and products in a chemical reaction. Such calculations are based on two laws of chemical combinations.

(*i*) Law of Conservation of Mass: Matter can neither be created nor destroyed during a chemical reaction. Since matter is atomic in nature, so *atoms can neither be created nor destroyed in a chemical reaction.* Thus it is concluded that the total number of atoms entering into a chemical reaction is equal to the total number of atoms of all the products.

(*ii*) Law of Definite Proportions: According to this law a pure chemical compound always contains the same elements combined in the same ratio by weight.

Moreover, stoichiometric calculations should be performed with two assumptions in hand.

(*i*) Reactants are completely converted to products.

(*ii*) No side reactions occur.

The following examples illustrate the idea.

Example

$$2\,H_2(g) + O_2(g) \xrightarrow[\text{discharge}]{\text{Electric}} 2H_2O\,(l)$$

or

2 molecules of H_2 + 1 molecule of $O_2 \longrightarrow$ 2 molecules of H_2O.

Similarly

2x molecules of H_2 + x molecules of $O_2 \longrightarrow$ 2x molecules of H_2O

So, the equation means that:

2 moles of H_2 + 1 mole of $O_2 \longrightarrow$ 2moles of H_2O

Wt. of 2moles of H_2 + Wt.of 1mole of $O_2 \longrightarrow$ Wt. of 2moles of H_2O

2 (2g) of H_2 + 2 (16g) of $O_2 \longrightarrow$ 2 (18g) of H_2O

36g of reactants $\longrightarrow$ 36g of products

Weight of reactants = Weigth of products

Example

$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

The above equation indicates that 2 moles of sodium hydroxide react with one mole of sulphuric acid to yield one mole of sodium sulphate and two moles of water. In other words from 2(23.0 + 16.0 + 1.0) = 80.0g of NaOH by reaction with H_2SO_4 yields (2 x 23.0) + 32.0 + (4 x 16.0) = 142.0g of Na_2SO_4. From any other amount of NaOH, the yield of Na_2SO_4 will be in a similar proportion to the number of moles taken.

1.13.1 Conversion Factors From the Balanced Equation

A balanced chemical equation can be usefully employed in calculations concerning chemical reactions i.e.;

In the synthesis of water from H_2 and O_2.

$$2\,H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l)$$

2 moles of water are produced for every 2 moles of H_2 used.

or

2 moles of water are produced for every 1 mole of O_2 consumed.

or

2 moles of H_2 are used up in the making of water for every 1 mole of oxygen.

So the coefficients present in the balanced chemical equation give us information about the quantitative relationship of various chemicals involved in the reaction.

Example 9

How many moles of water result from burning 4.7 moles of oxygen in an excess of H_2?

Solution

The term excess of H_2 means that sufficient quantity of H_2 is available for complete conversion of 4.7 moles of oxygen into water. We use the following relationship.

2 moles of H_2O is produced from 1 mole of O_2

So, 1 mole of oxygen produces 2 moles of water

Therefore, 4.7 moles of oxygen produce = 2 x 4.7 moles = 9.4 moles of H_2O.

Example 10

How many grams of potassium sulphate can be prepared from 28.0g of KOH according to the following equation.

$$2\,KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

Solution

The equation shows that for every mole of KOH which reacts, half as many moles of potassium sulphate are produced.

One mole of KOH weight = 56g.

Therefore, 28.0g KOH = 28.00/56.0 = 0.5 moles.

This much amount of KOH will produce 0.5/2 = 0.25 moles of K_2SO_4 (note half quantity of K_2SO_4 as compared to the moles of KOH used).

But one mole of K_2SO_4 = 174g.

Therefore, 0.25 moles of K_2SO_4 will produce 174 x 0.25 = 43.50g of K_2SO_4.

Example 11

A small piece of pure aluminium metal having volume of $1.250cm^3$ is reacted with an excess of hydrochloric acid. What is the weight of hydrogen liberated? (the density of aluminium is $2.70g/cm^3$.)

Solution

Before starting calculations for solving this problem we must write down first of all the reaction involved in this process.

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

Weight of Al = Volume x Density = $1.25cm^3 \times 2.70g/cm^3$ = 3.38g

$$\text{No. of moles of Al} = \frac{\text{Wt. in grams}}{\text{Wt. of one mole}} = \frac{3.38}{27} = 0.125$$

Now we know that

2 moles of Al = 3 moles of H_2

Therefore,

$$0.125 \text{ moles of Al} = \frac{3}{2} \times \frac{0.125}{1} = 0.1875 \text{ moles of } H_2$$

Wt. of hydrogen = 0.1875 mole x 2.02g/mol = 0.379g.

Example 12

H_2 gas is to be produced by the following reaction.

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

What is the minimum volume of a hydrochloric acid solution required to produce 10.0g of H_2. The hydrochloric acid solution is 27% by weight with a density of $1.14 g/cm^3$.

Solution

$$\text{No. of moles of } H_2 = \frac{10.00}{2.02} = 4.95$$

1 H_2 mole : 2 HCl moles

4.95 mole : 4.95 x 2 = 9.90 moles

Wt. of HCl = 9.90 x 36.5 = 361.4 g

27% of HCl solution by weight means that 27g of HCl is present in 100g of solution.

27g of HCl is available in 100 g of HCl solution.

Therefore,

$$361.4 \text{ g of HCl will be available in} = \frac{100}{27} \times 361.4 = 1338.5\text{g}$$

But Mass = Volume x Density

$$\text{or Volume} = \frac{\text{Mass}}{\text{Denstiy}}$$

Therefore, volume of HCl solution

$$= \frac{1338.5\text{g}}{1.14\text{g/cm}^3} = 1174.1 \text{ cm}^3$$

1.13.2 Applications of Limiting Reactants

We have discussed so far the stoichiometry of some simple and direct relationship in chemical equations. There are, however, some further points to be considered in this direction which are not comparatively simple. One aspect of such cases is the determination of the *"Limiting Reactant"*. When the

reactants are not mixed in stoichiometric amounts, then at the completion of reaction, some of the reactants are left unreacted. One of the reactants may be consumed earlier. This reactant is called limiting reactant. In order to identify the limiting reactant, the amounts of all reactants are converted to their moles. The molar amount of the required product is calculated from the molar amounts of all the reactants. That reactant which produces the least amount of product is the limiting reactant. Following example illustrates this principle.

Example 13

How much silver chloride will be formed by mixing 120.0g of silver nitrate with a solution of 52.0g of NaCl?

Solution

The chemical reaction is

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

As is evident from the equation given above one mole of silver nitrate reacts with one mole of sodium chloride to produce one mole of silver chloride.

$$\text{Amount of } AgNO_3 \text{ employed} = \frac{120.0\text{ g}}{170\text{ g/mol}} = 0.706 \text{ moles}$$

$$\text{Amount of NaCl employed} = \frac{52\text{ g}}{85.5\text{ g/mol}} = 0.89 \text{ moles}$$

From the above quantities it is evident that 0.706 moles of $AgNO_3$ will react with only 0.706 moles of NaCl to produce 0.706 moles of AgCl. Thus the amount of NaCl used is in excess. Hence $AgNO_3$ is limiting reactant. It will control the amount of AgCl produced.

Amount of AgCl formed = 0.706 moles x 143.4g/mole = 101.24g

Example 14

Sodium thiosulphate, $Na_2S_2O_3$ can be prepared by the reaction indicated below.

$$2Na_2S(aq) + Na_2CO_3(aq) + 4SO_2(g) \longrightarrow 3Na_2S_2O_3(aq) + CO_2(g)$$

If 100g each of the three reagents (Na_2S, Na_2CO_3, and SO_2) are reacted together, how many grams of $Na_2S_2O_3$ will be produced?

Solution

From the balanced equation we learn that the reactants must combine in the following ratio by weight.

2 moles of Na_2S : 1 mole of Na_2CO_3 : 4 moles of SO_2

Now converting the given quantities into moles.

No. of moles of Na_2S available $= \dfrac{100g}{78.0\ g/mol} = 1.28$

No. of moles of Na_2CO_3 available $= \dfrac{100g}{106\ g/mol} = 0.943$

No. of moles of SO_2 available $= \dfrac{100g}{64.1\ g/mol} = 1.56$

In order to determine the amount of $Na_2S_2O_3$, we perform calculations three times. The reactant which will give the minimum amount of $Na_2S_2O_3$ will be limiting and product so obtained will be our required answer.

From balanced chemical equation, we know that

(i)	Na_2S		$Na_2S_2O_3$
	2 moles	:	3 moles
	1 mole	:	3/2 moles
	1.28 moles		3/2x1.28=1.92 moles
(ii)	Na_2CO_3		$Na_2S_2O_3$
	1 mole	:	3 moles

	0.94 moles	:	3 x 0.94 = 2.82 moles
(*iii*)	SO_2		$Na_2S_2O_3$
	4 moles	:	3 moles
	1 mole	:	3/4 moles
	1.56 moles	:	3/4x1.56=1.17 moles

Since, SO_2 gives least number of moles of $Na_2S_2O_3$, so it is the limiting reactant.

Weight of $Na_2S_2O_3$ = Mol. wt x No. of moles

= 158 x 1.17 = 184.86 g

1.14 Reversible Reactions

We have considered so for such reactions that go to completion. This means that such a reaction proceeds in the direction of the arrow until one of the reactants i.e. *the limiting reactant* is consumed entirely, and the reaction stops. Calculations are made on the basis of the amount of limiting reactant.

However, in a large number of reactions, the products react among themselves to produce the original reactants. Such reactions are called *reversible reactions*. Reversible reactions are in a state of equilibrium indicated by single headed arrows. Following are a few important examples.

$$2\,SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5} 2\,SO_3\,(g)$$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$N_2(g) + 3H_2(g) \xrightleftharpoons{Fe_2O_3} 2NH_3(g)$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$$

$$CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O\text{–}H(aq) + C_2H_5OH \xrightleftharpoons{H_3O^+} CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O\text{–}C_2H_5 + H_2O(l)$$

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

In reversible reactions, reactants do not disappear completely. In reversible reactions the reactants are being produced from the products by reverse reaction and consequently a state of dynamic equilibrium is established. We cannot calculate the amount of product by the methods discussed above. For stoichiometry of such reactions some additional information is required. The stoichiometry of reversible reactions can be studied under the head, "chemical equilibrium". But we can make a passing remark here that if one of the products of a reversible reaction is removed continuously, the reaction can go to completion and hence calculations can be made. Such a situation is most common in those reactions where one of the products is either a gas that can easily escape or it is highly insoluble and precipitates out almost completely.

1.15 Theoretical and Actual Yields

In a chemical reaction certain amounts of products are obtained from the given amounts of reactants. The amounts of products obtained from the balanced chemical equation is regarded to as the theoretical yield. But as a matter of fact many chemical reactions do not proudce the amount of products expected theoretically. The reasons being (*a*) side reactions (*b*) reactions are reversible and, (*c*) mechanical loss of the product taking place during the course of separation and purification. For these reasons the actual yield is less than theoretical yield. Therefore, a chemist is often interested in knowing the % yield of a product which is given by following formula.

$$\% \text{ Yield} = \frac{\text{Actual yield obtained in practical work}}{\text{Theoretical yield (from equation of reaction)}} \times \frac{100}{1}$$

Example 15

Hydrazine, N_2H_4 (used as a fuel in rockets) can be produced by the following reactions.

$$Cl\,NH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$$

On reacting 2.00 kg Cl NH_2 with a large excess of NH_3, 946g N_2H_4 is obtained. What is the precentage yield of this reaction.

Solution

To determine the percent yield we require to know both the theoretical and actual yields of the reaction.

(i) *Theoretical yield:* According to the above reaction

$$\begin{array}{ccc} ClNH_2 & = & N_2H_4 \\ 1 \text{ mole} & & 1 \text{ mole} \end{array}$$

$$\text{No. of moles of } ClNH_2 = \frac{2000 \text{ g}}{51.5} = 38.83 \text{ moles}$$

From the balanced equations:

Cl NH_2		N_2H_4
1 mole	:	1 mole
38.83 moles	:	38.83 moles

Mol.Wt. of N_2H_4 = 32 g/mol

Wt. of N_2H_4 produced = 38.83 x 32 = 1242.6 g

Theoretical yield = 1242.6 g

(ii) *Actual yield* of N_2H_4 = 946 g.

(iii) *Per cent yield*

$$\% \text{ yield of } N_2H_4 = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

$$= \frac{946}{1242.7} \times \frac{100}{1} = 76.1\%$$

EXERCISE

1. Write notes on the follwing:

   (*a*) Significant figures

   (*b*) Precision and accuracy in scientific work

   (*c*) Zero as a significant figure

   (*d*) Rounding off data

2. Define the following units:

   (*a*) Metre

   (*b*) Joule

   (*c*) Calorie

   (*d*) Metre cube

   (*e*) Kelvin scale of temperature.

3. How will you distinguish between the followings:

   (*a*) Calorie and Joule

   (*b*) m^3 & dm^3

   (*c*) Litre an dm^3

   (*d*) Mass and Weight

   (*e*) Empirical formula and molecular formula

   (*f*) Molecular weight and formula weight

4. Explain the following terms.

   (*a*) Formula unit

   (*b*) Simplest or empirical

   (*c*) Molecular formula

   (*d*) Avogadro's number.

(*e*) Mole

5. How many sulphur atoms are present in each of the following quantities?

(*a*) 1.5 mole S; (*b*) 2.0 mole S_8; (*c*) $5.0\text{x}10^{-3}$ mole of H_2S

(*d*) 0.40 mole of CS_2

Ans: (*a*) $9.0\text{x}10^{23}$ (*b*) $9.6\text{x}10^{24}$ (*c*) $3.0\text{x}10^{21}$ (*d*) $4.8\text{x}10^{23}$.

6. In a collection of $2.48\text{x}10^{26}$ molecules of C_2H_5OH, what is the number of moles of (*a*) C atoms (*b*) H atoms (*c*) O atoms?

Ans: (*a*) $8.24\text{x}10^{2}$ moles of C; (*b*) $2.47\text{x}10^{3}$ moles of H; (*c*) $4.12\text{x}10^{2}$ moles of O.

7. A piece of aluminium metal weights 70.0g. How many atoms are present?

Ans: 1.56×10^{24} atoms of Al.

8. A sample of $MgBr_2$ contains $3.62\text{x}10^{24}$ Br^- ions. Calculate the following?

(*a*) Number of Mg^{2+} ions present in the sample.

(*b*) Number of formula units of $MgBr_2$.

(*c*) The weight of the sample.

Ans: (*a*) $1.81\text{x}10^{24}$; (*b*) $1.81\text{x}10^{24}$; (*c*) $5.53\text{x}10^{2}$

9. The liquid $CHBr_3$ has a density of 2.89 g/cm^3. What volume of this liquid should be measured out to contain a total of $2.40\text{x}10^{24}$ molecules of $CHBr_3$?

Ans: 348.5 cm^3.

10. Which of the following statements are correct for the compound $C_6H_{12}O_6$? Explain your reasoning.

(*a*) the formula given is an empirical formula.

(*b*) the proportions of H and O atoms are the same as in water.

(*c*) the element present in highest percentage by weight is oxygen.

(*d*) the proportions of carbon and oxygen, by weight, are equal.

Ans: (*a*) false (*b*) true (*c*) ture (*d*) false.

11. The compound trinitrotoluene (TNT) has the formula $C_7N_3H_5O_6$. Determine:

(*a*) the total number of atoms in one formula unit.

(*b*) the ratio of O atoms to N atoms.

(*c*) the ratio by weight of hydrogen to carbon in the compound.

(*d*) the element present in the greatest proportion by weight.

Ans: (*a*) 21 (*b*) 6:3 (*c*) 5:84 (*d*) Oxygen.

12. Given the reaction

$3Fe(s) + 4H_2O_{(g)} \longrightarrow Fe_3O_4 + 4H_2(g)$

(*a*) How many moles of $H_2(g)$ can be produced by reacting 125g Fe with an excess of steam $[H_2O\ (g)]$?

(*b*) How many grams of H_2O would be consumed in the conversion of 110g of Fe to Fe_3O_4?

(*c*) In one particular reaction 3.20 mole of $H_2(g)$ was produced as a result of this reaction. How many grams of Fe_2O_3 must also have been produced?

Ans: (*a*) 2.98 mole; (*b*) 47.3g H_2O (*c*) 186g Fe_3O_4.

13. How many millilitres of a water solution of $KMnO_4$ containing 158g/L must be used to complete the conversion of 75.0g KI to iodine (I_2) by the reaction?

$2KMnO_4 + 10KI + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4$
$+ 5I_2 + 8H_2O$

Ans: 90.5 mL $KMnO_4$.

14. A mixture of magnesium carbonate and magnesium hydroxide is known to contain 30% of $MgCO_3$ and 70% $Mg(OH)_2$. How many grams of HCl are required to dissolve a 40.0g sample of this mixture?

$MgCO_3(s) + 2HCl(aq) \longrightarrow MgCl_2 + H_2O + CO_2(g)$

$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2 + 2H_2O$

Ans: 45.66 HCl.

15. A 5.00 ml sample of liquid benzene; C_6H_6 (d = 0.879 g/mL is burned completely yielding CO_2 and H_2O as the only products. The CO_2 formed is passed into a barium hydroxide solution and yields a precipitate of $BaCO_3$. How many grams of $BaCO_3$ are produced?

$CO_2(g) + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O$

Ans: 66.5 of $BaCO_3$.

16. Ammonia gas (NH_3) can be generated by heating together the solids NH_4Cl and $Ca(OH)_2$. If a mixture containing 100g of each of these solids is heated, how many grams of NH_3 are produced?

$2NH_4Cl(s) + Ca(OH)_2(s) \longrightarrow CaCl_2(s) + 2NH_3(g) +$
$2H_2O(g)$

Ans: 31.8g of NH_3.

17. Chlorine gas can be produced in the laboratory by the reaction indicated. If a 61.3 g sample 96% $K_2Cr_2O_7$ is allowed to react with 320ml of a hydrochloric acid solution having a density of 1.15g/cm^3 and containing 30% HCl, how many grams of Cl_2 are produced?

$$K_2Cr_2O_7 + 14\ HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

Ans: 43.0g of chlorine.

18. Fill in the blanks with suitable words:

(i) Atom ___________ the smallest particle of matter. (is/is not)

(ii) Solubility is a ___________ property. (physical/chemical)

(iii) Burning of wood involves ___________ change. (physical/chemical)

(iv) The word SI stands for ___________. (standard international/system internationale)

(v) nm is ___________ than μm. (less/greater)

(vi) One km has ___________ hm. (10/100/0.1)

(vii) m^3 is ___________ than dm^3, while cm^3 is ___________ than dm^3. (greater/less)

(viii) One litre is ___________ dm^3. (less than/equal to/greater than)

(ix) There ___________ difference of mass and weight on the surface of earth. (is/is no)

(x) Kgm^2s^{-2} is the SI unit of ___________. (energy/work)

(xi) Joule is ___________ than calorie. (smaller/bigger)

(xii) 0.0087 contains ___________ significant figures. (4/5/2)

(xiii) 0.0087 has ___________ significant zeros. (1/3/2)

(xiv) Mass is a ___________ quantity. (derived/basic)

(*xv*) The atomic weight of an element is usually expressed in ____________. (gram/ounce)

(*xvi*) The value of one a.m.u is ____________ g. (6.02×10^{23}/1.66×10^{-24})

(*xvii*) The accuracy of a measurement ____________ upon the number of significant figures. (depends/does not depend)

(*xviii*) The number of significant figures ____________ upon the size of the object to be measured with a given scale. (depends/does not depend)

(*xix*) The % of oxygen in an organic compound ____________ be measured directly. (can/cannot)

(*xx*) Dissociation of NH_3 is a ____________ reaction (irreversible/reversible).

(*xxi*) Reversible reactions are ____________ 100% by increasing temperature. (completed/not completed)

(*xxii*) Actual yield of a reaction ____________ be changed by changing reaction conditions. (can/cannot)

(*xxiii*) Stoichiometric calculations of a reaction give us ____________ yield. (actual/theoretical)

19. Explain the followings with reasons:

(*i*) The number of significant figures shows the accuracy of measurement.

(*ii*) Precision and accuracy should go side by side for perfect measurement.

(*iii*) NaCl has 58.5 a.m.u as formula weight but not the molecular weight.

(*iv*) Avogadro's number of atoms of different elements have different weights.

(*v*) Law of conservation of mass operates in chemcial reactions but law of conservation of volume may not be obeyed.

(*vi*) A limiting reactant controls the quantities of prodûcts in a chemical reaction.

(*vii*) The actual yield of a chemical reaction is usually less than the theoretical yield.

(*viii*) Number of moles of atoms of an element in molecules may or may not be equal to number of moles of compound.

2

GASES

2.1 Introduction

Matter exists in three states *gases, liquids and solids*. In gases molecules are present quite wide apart and can move freely in the space provided. Gases are the simplest form of matter. Therefore, the gaseous state is easy to study and the behaviour of gases can be generalized with the help of a few simple equations which relate pressure, volume, temperature, and their molar amounts.

The following properties of gases are noteworthy.

2.2 The physical Characteristics of the Gases

(i) **Colour and Odour:** A few gases are coloured; for example, nitrogen dioxide is reddish brown, and iodine vapours have a violet colour. Anything that we can smell can exist in gaseous state, because the

familiar gases like O_2, N_2, H_2 and He are colourless and odourless.

(ii) **Indefinite Volume:** The volume of a gas is equal to the volume of its container. The volume of the gas changes with the change of size of the container. So, gases do not possess any definite volume and shape and occupy all available space.

(iii) **Indefinite Shape:** Gases have no definite shape. They adopt the shape of the container in which they are stored.

(iv) **Compressibility and Expansion:** Gases can be compressed by increasing pressure and can expand by decreasing pressure. It is the property of gases to adjust volume to any degree when compressed or expanded. This property is due to the fact that gas molecules are separated far apart in empty spaces. When compressed by applying pressure, empty spaces are reduced. The molecules of gases can be separated to any extent by reducing pressure. When gases suddenly expand they cause cooling. This phenomenon is called the Joule-Thomson effect. This is of great practical importance in the liquefaction of gases on industrial scale.

(v) **Miscibility of Gases:** The molecules of gases can effuse and diffuse and are freely miscible provided they donot react chemically. The volume of a mixture of gases is independent of the original volumes of the individual gases.

(vi) **Effect of Temperature and Pressure:** Gases expand on heating and contract on cooling. The increase in temperature increases the kinetic energy of gas molecules and increase of pressure on the walls of vessel. This leads to expansion of gases. The collisions on the walls are less intense at lower

temperature. So due to this phenomenon gases contract on cooling.

(vii) **Gases Exert Pressure:** A gas exerts pressure either alone or in a mixture. In a mixture of gases, each gas exerts the same pressure that it would exert if present alone. The total pressure of a mixture of gases is the sum of their partial pressures.

2.2.1 Pressure and its Measurement

Gaseous pressure is the force exerted by gas molecules on a unit area. The SI unit for measurement of pressure is Pascal (Pa). One Pascal is one Newton per square metre or $1\ Nm^{-2}$. This is relatively a small pressure unit. Other units for measurement of pressure are torr, or mm Hg and standard atmospheric pressure (atm). In order to understand these units let us study the pressure exerted by the atmosphere and its measurement with the help of a barometer.

Barometer is used to measure pressure. A simple barometer is a glass tube of about one metre in length and sealed at one end. The tube is filled with mercury and inverted in a dish of mercury by placing thumb on the open end of the tube. The mercury level falls in the tube due to gravity (Fig. 2.1) and stays at a particular height or level. The staying of mercury at certain height (h) is due to atmospheric pressure exerted by air on mercury in the dish. The height of mercury is measured in millimetres (mm) of Hg (or torr) to determine pressure of the atmosphere. The height of mercury column changes with temperature of the

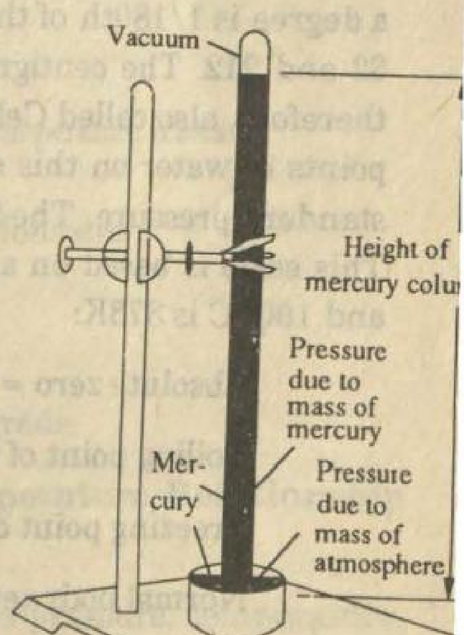


Fig. 2.1 — A Mercury Baromete

atmosphere. It is therefore, necessary to specify temperature at which the pressure is being measured.

Standard pressure of 76cm or 760mm Hg or 760 torr is called one atmosphere (1 atm). It is the force exerted by 76cm long column of mercury on an area of 1 cm^2 at 0°C. It is the average pressure of atmosphere at sea level.

The various units of pressure are indicated below.

1 mm Hg	= 1 torr
1 atmosphere	= 760 torr
	= 14.7 PSi (pounds per square inch)
	= 101325 Pa (Pascal)
	= 1.01325 bar

2.2.2 Scales of Temperature

Three temperature measuring scales are in common use. One is Fahrenheit scale in which freezing point of water is taken as 32°F and boiling point of water as 212°F. On this scale a degree is 1/180th of the distance between the fixed points. i.e., 32 and 212. The centigrade scale was proposed by Celsius. It is therefore, also called Celsius scale (°C). The freezing and boiling points of water on this scale are 0°C and 100°C respectively at standard pressure. The SI scale used in scientific work is Kelvin. This scale is based on absolute temperature. Thus 0°C is 273K and 100°C is 373K:

Absolute zero = 0 K or −273.15°C or −459.7°F

Boiling point of water = 373K or 100°C or 212 °F

Freezing point of water = 273K or 0°C or 32°F

Normal body temperature = 310K or 37°C or 98.6°F.

In order to provide a uniform basis for comparing volumes and other properties of gases that vary with temperature, it has been found convenient to select 273.15K as the standard temperature.

In all scientific work the pressure 760 torr (1 atmosphere) and the temperature 273K are known collectively as standard conditions of temperature and pressure.

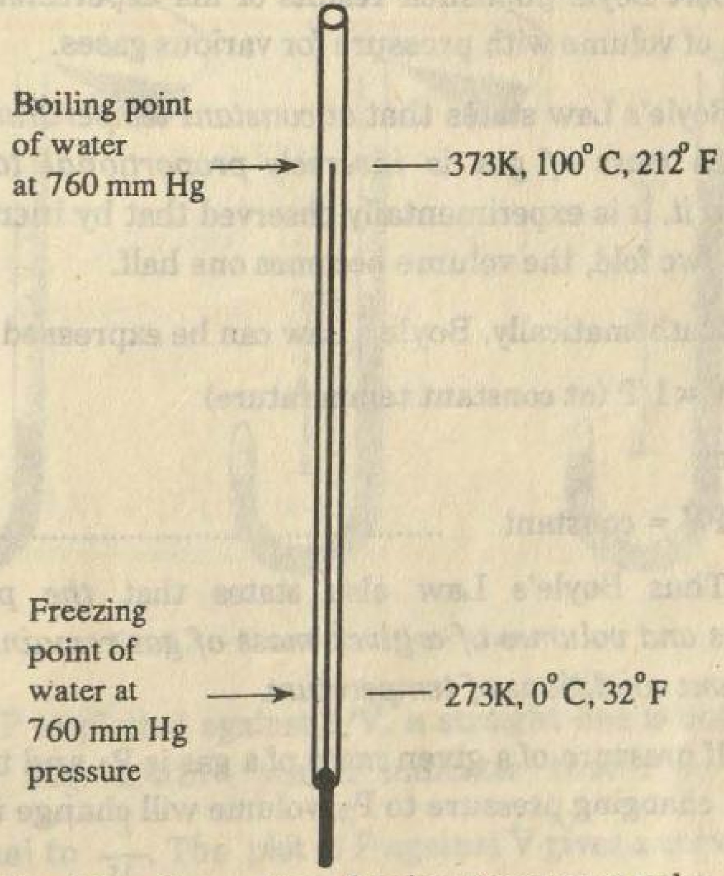


Fig. 2.2 — Comparision of various temperature scales.

Formulae used for interconversions are :

$$\text{Centigrade } C = \frac{5}{9}(F - 32)$$

$$\text{Kelvin } K = 273.15 + \text{Centigrade}$$

2.3 Volume, Pressure and Temperature Relationship — The Gas Laws

The behaviour of gases towards pressure, temperature, volume and molar amount can be generalized by gas laws i.e. Boyle's Law, Charles's Law and General Gas Law.

2.3.1 Boyle's Law

Gases have a characteristic property of compressibility and expansion. This behaviour is summarised in Boyle's Law. In 1662 Robert Boyle published results of his experiments on the variation of volume with pressure for various gases.

Boyle's Law states that *at constant temperature, volume of a given mass of gas is inversely proportional to pressure exerted on it*. It is experimentally observed that by increasing the pressure two fold, the volume becomes one half.

Mathematically, Boyle's Law can be expressed as:

$V \propto I/P$ (at constant temperature)

or

$PV = \text{constant}$ .... (2.1)

Thus Boyle's Law also states that *the product of pressures and volumes of a given mass of gas remains constant under same conditions of temperature.*

If pressure of a given mass of a gas is P_1 and the volume V_1, then changing pressure to P_2, volume will change to V_2, such that:

$P_1V_1 = P_2V_2$ (provided the temperature before and after the change remains constant).

2.3.2 Experimental Verification of Boyle's Law

The apparatus used for the verification of Boyle's Law consists of a J tube. One end of J tube is closed and graduated. A given mass of gas is enclosed in the graduated closed limb of the J tube (Fig. 2.3). The pressure on gas is changed by raising the mercury level in the open limb. The difference in height of mercury, 'h' in J tube is measured. The pressure exerted over the gas in closed limb will be equal to atmospheric pressure (barometric pressure in mm of Hg) plus 'h' mm of Hg. The volume at various pressures is also noted. It is observed that the product of pressure and volume before and

after the change remains almost constant at the same temperature.

PV = constant

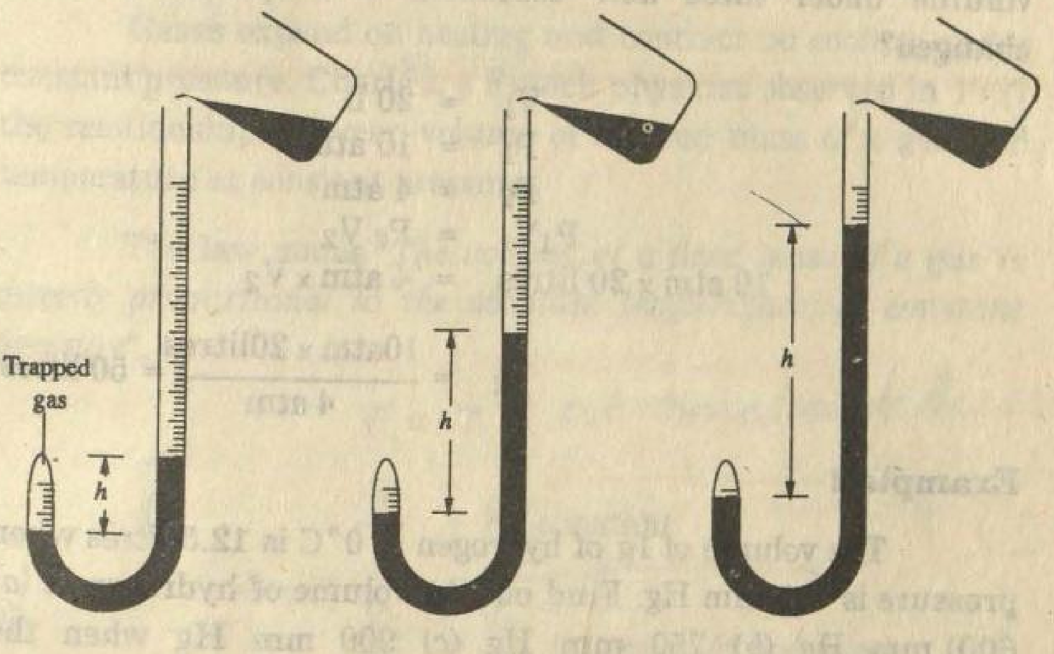


Fig. 2.3 — Illustrations of Boyle's Law.

If P is plotted against 1/V, a straight line is obtained as shown in Fig. 2.4(b) which indicates that P is directly proportional to $\frac{1}{V}$. The plot of P against V gives a curve called Isotherm.

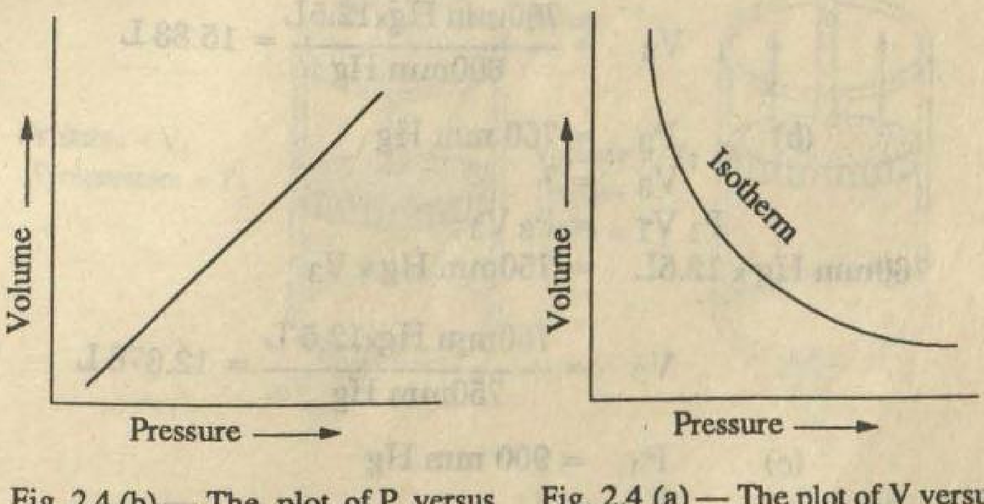


Fig. 2.4 (b) — The plot of P versus 1/V is a straight line which indicates a direct relationship between P and 1/V at a given temperature.

Fig. 2.4 (a) — The plot of V versus P does not indicate a direct relationship between pressure and volume at a given temperature.

Example 1

A 20 litre sample of a gas at 0°C and 10 atm pressure is allowed to expand until its pressure is 4.0 atm. What will be the volume under these new conditions if temperature is not changed?

$$V_1 = 20\text{ L}$$
$$P_1 = 10\text{ atm}$$
$$P_2 = 4\text{ atm}$$
$$P_1V_1 = P_2V_2$$
$$10\text{ atm} \times 20\text{ litres} = 4\text{ atm} \times V_2$$
$$V_2 = \frac{10\text{atm} \times 20\text{litres}}{4\text{ atm}} = 50\text{ litres}$$

Example 2

The volume of 1g of hydrogen at 0°C is 12.5 litres when pressure is 760 mm Hg. Find out the volume of hydrogen at (*a*) 600 mm Hg (*b*) 750 mm Hg (*c*) 900 mm Hg when the temperature is kept constant.

(a) $P_1 = 760\text{ mm Hg}$ $\quad P_2 = 600\text{mm}$

$V_1 = 12.5\text{ litres}$ $\quad V_2 = ?$

$$P_1V_1 = P_2V_2$$
$$760\text{mm Hg} \times 12.5\text{ L} = 600\text{ mm Hg} \times V_2$$
$$V_2 = \frac{760\text{mm Hg} \times 12.5\text{L}}{600\text{mm Hg}} = 15.83\text{ L}$$

(*b*) $P_3 = 750\text{ mm Hg}$

$$V_3 = ?$$
$$P_1V_1 = P_3V_3$$
$$760\text{mm Hg} \times 12.5\text{L} = 750\text{mm Hg} \times V_3$$
$$V_3 = \frac{760\text{mm Hg} \times 12.5\text{ L}}{750\text{mm Hg}} = 12.676\text{ L}$$

(*c*) $P_4 = 900\text{ mm Hg}$

$$V_4 = ?$$
$$P_1V_1 = P_4V_4$$
$$760\text{mm Hg} \times 12.5\text{L} = 900\text{mm Hg} \times V_4$$

$$V_4 = \frac{760\text{mm Hg} \times 12.5\text{ L}}{900\text{mm Hg}} = 10.56\text{ L}$$

2.3.3 Charle's Law

Gases expand on heating and contract on cooling under constant pressure. Charle's, a French physicist observed in 1787 the relationship between volume of a given mass of a gas and temperature at constant pressure.

The law states "*The volume of a fixed mass of a gas is directly proportional to the absolute temperature, at constant pressure*".

$$V \propto T$$

$$\frac{V}{T} = K \text{ constant}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (at constant pressure)} \qquad (2.2)$$

T is temperature in Kelvin.

The Charle's Law can be verified as shown in Fig. 2.5. It

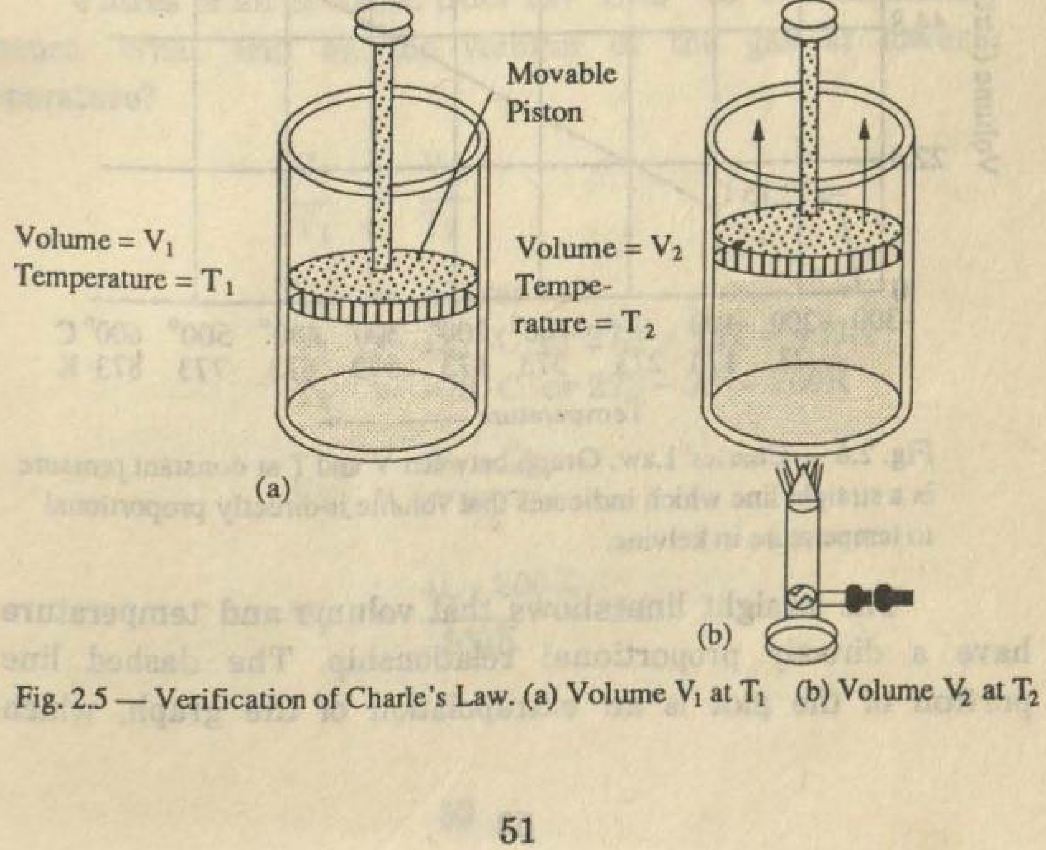


Fig. 2.5 — Verification of Charle's Law. (a) Volume V_1 at T_1 (b) Volume V_2 at T_2

may be noted that volume of a given mass of a gas increases with rise of temperature.

2.3.4 Absolute Zero:

In order to understand the absolute zero of temperature scale, we should consider the following quantitative statement of Charle's Law.

The volume of a given mass of an ideal gas increases or decreases by 1/273 of its original volume at 0 °C by increasing or decreasing temperature by 1 °C at constant pressure.

According to this statement the volume of given mass of a gas should be zero at −273 °C. Let us consider one mole of an ideal gas at atmospheric pressure. When its temperature is varied, its volume changes.

If volume of a given mass of a gas is plotted against temperature at constant pressure, the plot shown in Fig. 2.6 is obtained.

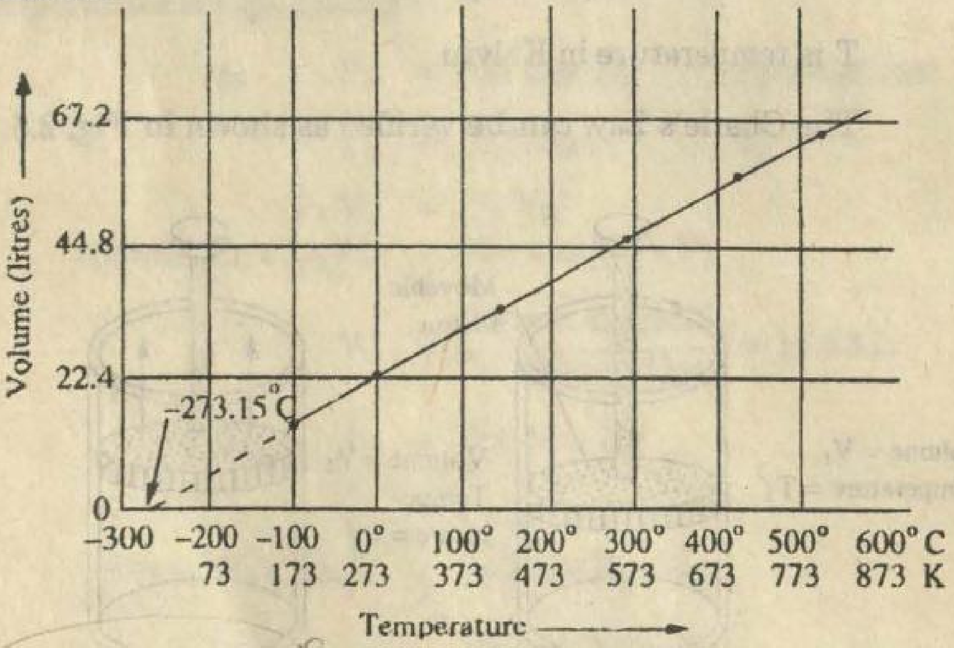


Fig. 2.6 — Charles' Law. Graph between V and T at constant pressure is a straight line which indicates that volume is directly proportional to temperature in kelvins.

The straight line shows that volume and temperature have a directly proportional relationship. The dashed line portion of the plot is an extrapolation of the graph, which

illustrates a logical conclusion from the observations that when the gas is cooled to −273.15°C, it should disappear entirely. The exact value of absolute zero from this graph comes out to be −273.15°C. However, for routine calculations, the value of absolute zero is taken as −273°C. We know from experiments that this does not happen. Instead Charles' Law becomes a less and less accurate description of gas behaviour as the temperature decreases. In other words at lower temperatures, the gases do not obey the gas laws mentioned above, because the velocities of molecules decrease and spaces between them become smaller, and as a result the gas liquifies or solidifies. The temperature at which broken line reaches zero volume, is −273.15°C and is independent of the nature of the gas used in the experiment. The value −273.15°C is designated as absolute zero, or zero of the Kelvin scale.

$$-273.15\,^\circ C = 0.0K$$

$$\text{or} \quad 0\,^\circ C = 273.15K$$

For simplification in calculations we can take -273°C as equal to 0K.

Example 3

4 litres of air is cooled from 127°C to −73°C at constant pressure. What will be the volume of the gas at lower temperature?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 4 \text{ litres}$$

$$T_1 = 127^\circ C \text{ or } 273 + 127 = 400K$$

$$T_2 = -73^\circ C \text{ or } 273 - 73 = 200K$$

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{4L \times 200K}{400K} = 2\,L$$

2.3.4 Ideal or General Gas Equation

The three variables volume, pressure and temperature can be interrelated in one expression.

According to Boyle's Law, for a given mass of a gas, say n moles, volume is inversely proportional to pressure at constant temperature.

$$V = \text{constant} \times \frac{1}{P}, \text{ at fixed T and n.}$$

Charle's Law states that volume of given mass of a gas is directly proportional to temperature when pressure is kept constant.

$$V = \text{constant} \times T, \quad \text{at fixed P and n.}$$

We also know that at constant temperature and constant pressure the volume is proportional to the mass of the gas. That is,

$$V = \text{constant} \times n$$

Where n is mass of a gas in terms of number of moles of a gas, these proportionalities combine to give a single relationship.

$$V = \text{constant} \times \frac{1}{P} \times T \times n$$

or

$$PV = \text{constant} \times T \times n$$

or

$$PV = RTn$$

or

$$PV = nRT \qquad \text{.......................................} (2.3)$$

Where R is a constant known as universal gas constant and equation (2.3) is known as the general gas equation.

or

$$\frac{PV}{T} = nR$$

If P, V and T are changed for a gas from P_1, V_1 and T_1 to P_2, V_2 and T_2, following relationship holds.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R \quad \text{.............................. (2.4)}$$

Since $$n = \frac{W}{M} = \frac{\text{weight}}{\text{Mol. Wt.}}$$

so equation 2.3 becomes

$$P V = \frac{W}{M} RT \quad \text{.................................... (2.5)}$$

or

$$M = \frac{WRT}{PV} \quad \text{.................................. (2.6)}$$

So, molecular weight can be determined, if P, V, W and T are known.

Equation (2.5) can be rearranged as

$$PM = \frac{W}{V} RT$$

Where $$\frac{W}{V} = \text{density (d)}$$

Hence $$PM = d\,RT$$

or $$d = \frac{PM}{RT} \quad \text{.................................. (2.7)}$$

So, knowing, P, T and molecular weight of a gas, its density can be calculated.

2.3.5 Units and Value of R

Numerical value of the gas constant R is totally independent of the nature of the gas but depends on the initial values of P, V and T. The value of R is calculated for one mole of gas at standard conditions of temperature and pressure or STP

(T = 0°C or 273K and P = 760 mm Hg or 1 atm). Under standard conditions of temperature and pressure one mole of a gas occupies 22.4 litres.

$$n = 1.0 \text{ mole} \qquad T = 0°C \text{ or } 273K$$

$$P = 1 \text{ atm} \qquad V = 22.4 \text{ L}$$

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4\text{L}}{1 \text{ mole} \times 273 \text{ K}}$$

$$R = 0.08205 \text{ L. atm mole}^{-1} \text{ K}^{-1} \qquad \text{.............} (2.8)$$

If pressure is expressed in Newtons per metre square (Nm^{-2}) and V in cubic metres (m^3) (both SI units), we find that

$P = 101300 \; Nm^{-2}$ (equal to 1 atm)
$V = 0.0224 \; m^{-3}$ (since $1 \; L = 10^{-3} m$)
so $22.4L = 0.0224 m^{-3}$
$n = 1$ (one mole of gas)
$T = 273 \; K$

$$R = \frac{101300 \; Nm^{-2} \times 0.0224 \; m^3}{1 \text{ mole} \times 273 \text{ K}}$$

$$= 8.3143 \; Nm \; K^{-1} \; mol^{-1} = 8.3143 \; JK^{-1} \; mol^{-1} \quad .. (2.9)$$

Since We know that;

1 calorie = 4.18 J, the vlaue of R may be expressed in calories.

$$\therefore \quad R = \frac{8.3143}{4.18} = 1.987 \text{ cal } K^{-1} \text{ mol}^{-1} \qquad \text{.................} (2.10)$$

This tells us that units of R are expressed in energy $K^{-1} \; mol^{-1}$.

It must be noted that this general gas equation is obeyed by an ideal or perfect gas defined as the one which strictly obeys the gas laws (Boyle's and Charles' Laws) at all temperatures and pressures. In actual practice no gas is ideal or perfect. Such gases are non ideal gases which do not obey the gas equation rigidly. The gases at sufficiently high temperature above their B.P. start obeying the gas laws. At ordinary temperature, the

most nearly ideal gases are N_2, He and H_2 which have very low boiling points.

Example 4

5-litres of a gas at 273°C and 2 atm. is cooled to 0°C and its pressure changes to 1 atm. What will be the new volume under these conditions?

Solution

$$V_1 = 5 \text{ litres}$$
$$P_1 = 2 \text{ atm}, \quad P_2 = 1 \text{ atm}$$
$$T_1 = 273 + 273^{\circ}C = 546K$$
$$T_2 = 0^{\circ}C + 273 = 273K$$
$$V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$V_2 = \frac{2 \text{ atm} \times 5L}{546 \text{ K}} \times \frac{273 \text{ K}}{1 \text{ atm}} = 5L$$

Example 5

What is the weight of 10 litres of CO_2 at 27°C and 5 atmospheric pressure?

Solution

$$P = 5 \text{ atmospheres}$$
$$V = 10 \text{ L}$$
$$W = ?$$
$$T = 27 + 273 = 300 \text{ K}$$
$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$
$$M = 44 \text{ g mol}^{-1}$$

Formula used : $$PV = \frac{W}{M} RT$$

$$5 \times 10 = \frac{W}{44} \times 0.0821 \times 300$$

$$\text{Wt. of gas} = W = \frac{5\text{ atm} \times 10\text{L} \times 44\text{g mol}^{-1}}{0.0821\text{ L atm K}^{-1}\text{mol}^{-1} \times 300\text{K}} = 89.3\text{g}$$

Example 6

What is the density in grams/litre of SO_2 at 20°C and 750mm Hg pressure?

Solution

$$P = 750\text{mm Hg} = \frac{750}{760}\text{ atm.} = 0.98\text{ atm},$$

$$T = 20^\circ C + 273 = 293K$$

$$M = SO_2 = 64\text{ g mol}^{-1}$$

$$R = 0.0821\text{ L atm. K}^{-1}\text{ mol}^{-1}$$

$$d = ?$$

Formula used: $$d = \frac{MP}{RT}$$

$$\therefore \quad d = \frac{64\text{gmol}^{-1} \times 0.98\text{ atm}}{0.0821\text{L atm K}^{-1}\text{mol}^{-1} \times 293\text{K}} = 2.60\text{ g/L}$$

2.4 Diffusion and Effusion of Gases

Gases have the property of mixing with one another. If a jar of air is inverted over a jar of carbon dioxide, both gases will mix together to form a homogeneous mixture. This spontaneous mixing of molecules of different gases by random motion and collisions until the mixture becomes homogeneous is called gaseous diffusion.

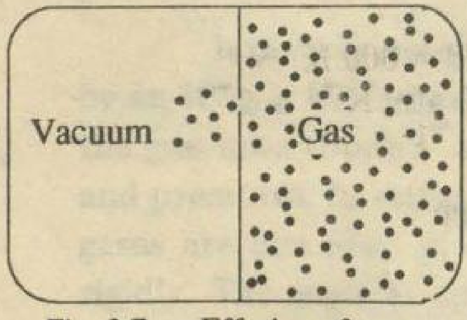


Fig. 2.7 — Effusion of a gas.

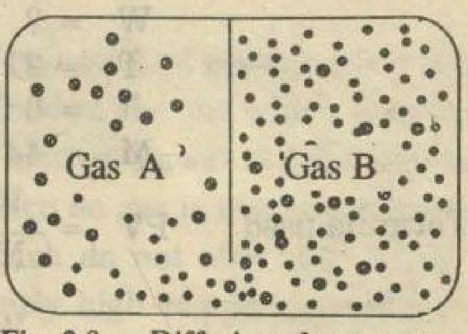


Fig. 2.8 — Diffusion of two gases.

Another related property of gases is effusion. Effusion is the escape of gas molecules one by one, without collisions through a hole of molecular dimensions. Effusion is of interest as it provides a method for determining molecular masses.

Experiment

Fit up a porous pot P,with a bent tube containing a bulb in between. The bent tube is filled with coloured water. On lowering cylinder C, containing hydrogen gas a water fountain F, is observed. This is because hydrogen is lighter than air and can diffuse more quickly. Therefore, it enters the porous pot much quicker than heavier air molecules can come out. Hence pressure inside the pot increases, and water is forced out in the form of a fountain.

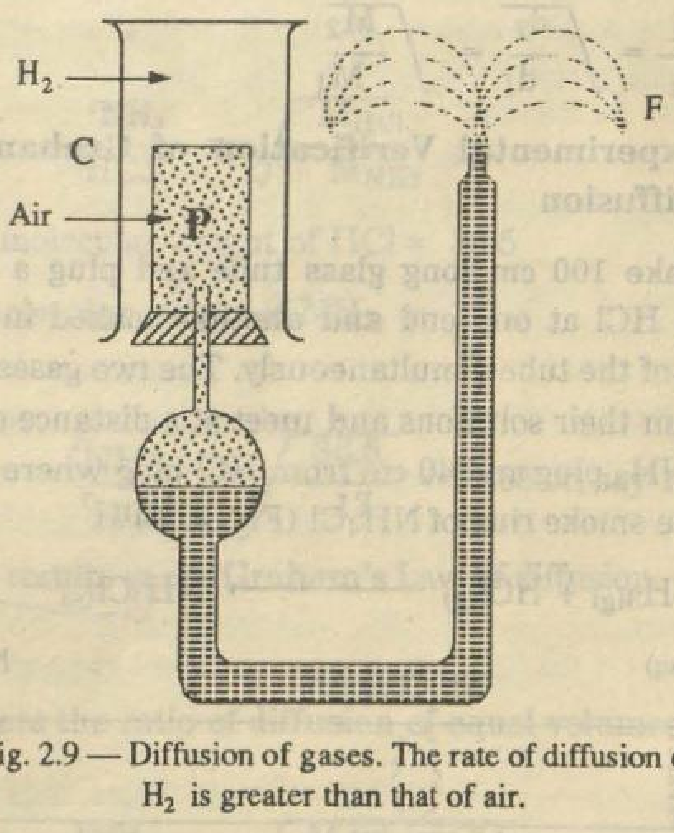


Fig. 2.9 — Diffusion of gases. The rate of diffusion of H_2 is greater than that of air.

2.4.1 Graham's Law of Diffusion and Effusion of Gases

The role of diffusion of gases is governed by Graham's Law which may be stated as under:

"The rates of diffusion of two gases are inversely proportional to the square roots of their densities, or molecular weights at the same pressure and temperature".

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{.................................... (2.11)}$$

Where r_1 and r_2 are the rates of diffusion of two gases, d_1 and d_2 are the gas densities and M_1 and M_2 are molecular weights of two gases.

Graham's law of effusion is also stated in a similar way: *The rates of effusion of two gases at the same pressure and temperature are inversely proportional to the square root of their densities or molecular weights*, i.e.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

2.4.2 Experimental Verification of Graham's Law of Diffusion

Take 100 cm long glass tube and plug a cotton swab soaked in HCl at one end and another soaked in NH_3 at the other end of the tube simultaneously. The two gases are found to escape from their solutions and meet at a distance of roughly 60 cm from NH_3 plug and 40 cm from HCl plug where they react to form white smoke ring of NH_4Cl (Fig. 2.10)

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$

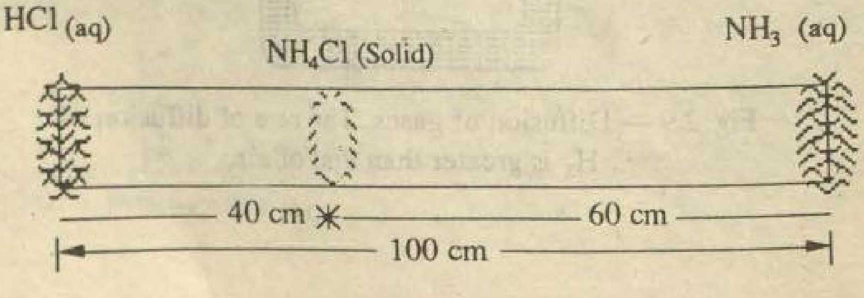


Fig. 2.10

The ratio of velocities of two gases depends on their distance travelled by the respective gases.

$$\frac{\text{velocity of } NH_3}{\text{velocity of } HCl} = \frac{\text{distance covered by } NH_3}{\text{distance covered by } HCl}$$

$$= \frac{60}{40} = 1.5$$

This ratio indicates the relative rate of diffusion of two gases which may be calculated on the basis of Graham's Law of diffusion. Density of HCl = $1.66 gL^{-1}$ and of NH_3 = $0.76 gL^{-1}$

$$\frac{\text{rate of diffusion of } NH_3}{\text{rate of diffusion of } HCl} = \sqrt{\frac{\text{density of } HCl}{\text{density of } NH_3}}$$

$$= \sqrt{\frac{1.66}{0.76}} = 1.48$$

Which is nearly equal to 1.5

Similarly,

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

Since molecular weight of HCl = 36.5

and molecular weight of NH_3 = 17

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{36.5}{17}} = 1.465 \text{ or, say } 1.5$$

These results verify Graham's Law of diffusion.

Example 7

Calculate the ratio of diffusion of equal volumes of NH_3 and CO_2

$$\frac{r_{NH_3}}{r_{CO_2}} = \sqrt{\frac{\text{M.wt. of } CO_2}{\text{M.wt. of } NH_3}}$$

$$= \sqrt{\frac{44}{17}} = 1.6$$

Rate of diffusion of NH_3 is 1.6 times faster than CO_2.

2.5 Dalton's Law of Partial Pressures

Air is a mixture of several gases. In this mixture nitrogen is 78.08% and is relatively unreactive. Oxygen makes up about 20.95% of the air and is essential for life. The noble gas argon is roughly 0.93% of the total volume of air and carbon dioxide is present to the extent of 0.03%. A large number of other gases are also present in even small amounts in clean dry air.

In air, the pressure of each gas contributes to the total pressure (P) of the mixture. The pressure of each gas in the mixture is called partial pressure of that gas. According to Dalton's Law of partial pressures;

"The total pressure exerted by a mixture of gases is sum of the partial pressures of all the gases present".

$$P = p_1 + p_2 + p_3 \text{ etc.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.12)$$

In air

$$P_{atm} = PN_2 + PO_2 + p_{Ar} + PCO_2 + p_{trace\ gases}$$

The greater the amount of a gas present in the mixture of gases, greater would be the partial pressure exerted by that gas. In other words, more molecules of a gas are present in the gaseous mixture, more pressure is exerted by that gas. It is because

$$\frac{PV}{T} = nR \text{ (general gas law or ideal gas equation)}$$

or $$P = \frac{n(RT)}{V} \text{ (n = number of moles of gas)}$$

As R, T and V for all the gases of the mixture are the

same, therefore, $\frac{RT}{V}$ will be a constant quantity. However, n is different for different gases, therefore,

$$P \propto n. \qquad \text{..................(2.13)}$$

So, pressure P is directly proportional to the number of moles of a gas.

2.5.1 Practical Applications of Dalton's law of Partial Pressures

Dalton's Law of partial pressure is of wide applicability and some of the practical applications of Dalton's law are given below:-

1. The respiration process taking place in living things depends on differences in partial pressures. Oxygen moves from the air, where its partial pressure is relatively high (159g/cm^2) to the lungs where its partial pressure is lower (116/cm^2). The carbon dioxide, which is the waste product of respiration, moves in the opposite direction and is exhaled into the atmosphere.

2. The partial pressure of oxygen in air is 159g/cm^2. One feels comfortable in respiration process at this partial pressure of oxygen. At high altitude the pilots may have uncomfortable breathing in a non-pressurized cabin where oxygen partial pressure is around 150g/cm^2.

3. Deep sea divers breathe air under increased pressure. This increased pressure of air is due to the pressure exerted by water. For example, they breathe at five times the normal pressure at a depth of 40 metres. Regular air cannot be used in divers' tanks, because the partial pressure of oxygen would be 750mm in that case. Therefore, deep sea divers breathe a mixture of 96% N_2 and 4% O_2. The partial pressure of this oxygen in mixture of gases will be just around the required limits.

4. Gases are usually collected over water. Due to vaporization, part of water mixes with the gas as water vapour.

Such observations are summed up in Gay-Lussac's law of combining volumes which states, "the volume of reactant and product gases at a given temperature and pressure are in ratios of small whole numbers." His results were based on some experiments on reaction of gases.

Avogadro interpreted Gay-Lussac's law of combining volumes in terms of what we now call Avogadro's law, which states, "*Equal volumes of all gases at the same temperature and pressure contain equal number of molecules*".

Since equal number of molecules mean equal number of moles, and since the number of moles of any gas is related directly to its volume, i.e.

$$V \propto n$$

therefore, we expect one mole of all gases to occupy the same volume at given temperature and pressure.

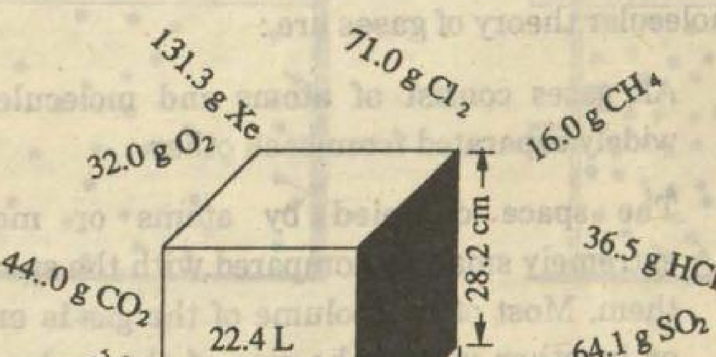


Fig. 2.11— One mole of a gas occupies 22.4L at STP.
The weight given for each gas is the weight of one mole.

One mole of any gas contains the same number of molecules (Avogadro's number = 6.022×10^{23} determined on the

basis of experimental observations) and by Avogadro's law every gas must occupy the same volume at a given temperature and pressure. The volume occupied by one mole of a gas is called the molar gas volume (Fig. 2.11)

It is found that one mole of an ideal gas at S.T.P. occupies a volume of 22.4litres.

1 mole of O_2 = 22.4 litres at S.T.P. = 32g O_2 = 6.022 x 10^{23} oxygen molecules

1 mole of CO_2 = 22.4 litres at S.T.P. = 44gCO_2 = 6.022 x 10^{23} CO_2 molecules.

2.7 The Kinetic Molecular Theory of Gases

The physical behaviour of gases as described by gas laws was explored in the eighteenth and nineteenth centuries. A theory known as *kinetic molecular theory* was later developed to explain the physical behaviour of gases. The main postulates of kinetic molecular theory of gases are :

(i) All gases consist of atoms and molecules that are widely separated from each other.

(ii) The space occupied by atoms or molecules is extremely small as compared with the space between them. Most of the volume of the gas is empty space or in other words the size of the molecule is very small as compared to the distance between them.

(iii) Gas molecules are in constant random motion in straight lines. The direction of their motion changes only when they collide with another molecule or with the walls of the container. Pressure exerted by a gas is due to collisions of molecules on walls of the containers.

(iv) There are no attractive forces between the molecules of a gas. When molecules collide with each other, they do not lose any kinetic energy. The collisions are

thus said to be perfectly elastic. The collision without any gain or loss of energy is called elastic collision.

(*v*) The average speed and average kinetic energy of gas molecules are directly proportional to the Kelvin temperature.

(*vi*) At the same temperature, the molecules of every gas have the same average kinetic energy.

(*vii*) Force of gravity has almost no influence on the molecules of gas.

Explanation of Gas Laws on Kinetic Theory

1 - Boyle's Law

At constant temperature, the molecules move with the same average speed and collide with one another as well as the walls of the container. Number of molecular collisions per unit walls area per second determine the pressure of a gas. When

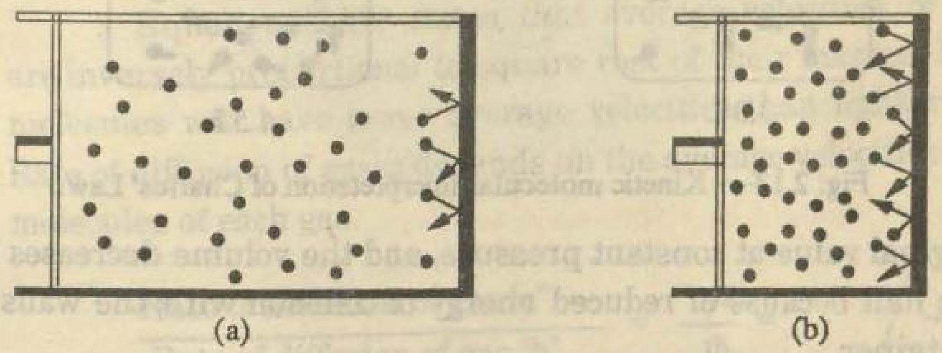


Fig. 2.12 — When volume of a gas is halved on going from (a) to (b) twice as many molecules collide each second with the walls and that doubles the pressure.

volume of a particular amount of a gas is reduced to one half, the molecules would collide with the walls of the container more frequently. Hence wall receives more collisions per second and observed pressure is greater.

2 - Charles' Law

The average kinetic energy of gas molecules is directly proportional to absolute temperature. Doubling the temperature of a gas doubles the average kinetic energy of the molecules, and the increased force of collisions of molecules with the walls doubles the volume at constant pressure. Similarly, halving the absolute temperature decreases kinetic energy to one half of its

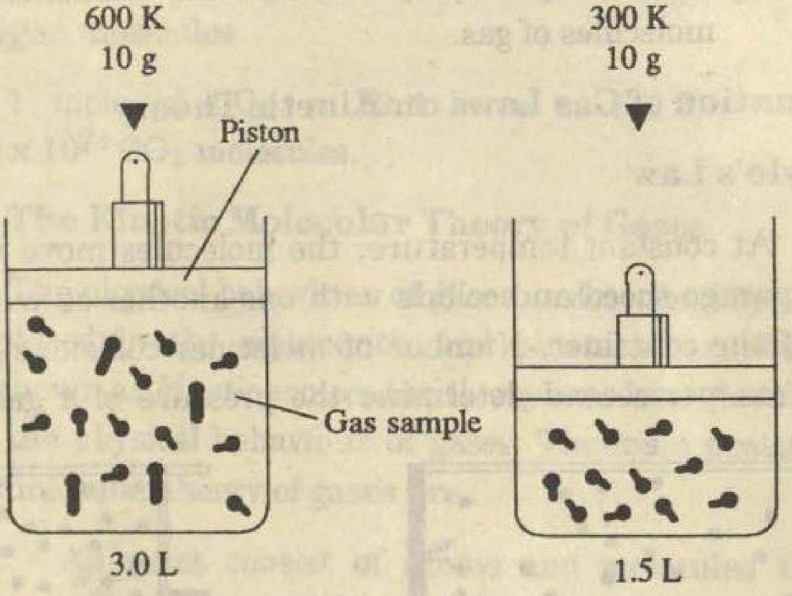


Fig. 2.13 — Kinetic molecular interpretation of Charles' Law.

original value at constant pressure, and the volume decreases by one half because of reduced energy of collision with the walls of container.

3 - Daltons's Law of Partial Pressure

In mixture of gases, the number of elastic collisions of each gas on the walls of the container will depend on the number of its molecules and would remain unaffected on mixing with other gases. The total number of elastic collisions with walls of the container will depend on the sum of the collisions of molecules of each gas.

4 - Graham's Law of Diffusion

According to the kinetic molecular theory the molecules of every gas have the same average kinetic energy at the same

temperature. So average kinetic energies of gas molecule 'a' and gas molecule 'b' at the same temperature should be equal.

$$\tfrac{1}{2} m_a u^2_a = \tfrac{1}{2} m_b u^2_b \quad \text{.................(2.14)}$$

Where m_a and m_b are masses and u_a and u_b are average velocities of gases a and b, respectively.

Equation (2.14) can be re-written as,

$$\frac{u^2_a}{u^2_b} = \frac{\tfrac{1}{2} m_b}{\tfrac{1}{2} m_a}$$

$$\frac{u^2_a}{u^2_b} = \frac{m_b}{m_a}$$

or

$$\frac{u_a}{u_b} = \sqrt{\frac{m_b}{m_a}} \quad \text{...............(2.15)}$$

Equation (2.15) states that average velocities of gases are inversely proportional to square root of their masses. Heavy molecules will have lower average velocities than lighter ones. Rate of diffusion of gases depends on the average velocities of the molecules of each gas.

$$\frac{\text{Rate of diffusion of gas 'a'}}{\text{Rate of diffusion of gas 'b'}} = \frac{u_a}{u_b} = \sqrt{\frac{m_b}{m_a}}$$

But molecular weights (M) are numerically equal to masses (m) of molecules. Therefore,

$$\frac{r_a}{r_b} = \sqrt{\frac{M_b}{M_a}}$$

Since molecular weights are directly proportional to densities, therefore,

$$\frac{r_a}{r_b} = \sqrt{\frac{d_b}{d_a}}$$

This is the expression of Graham's law of diffusion of gases.

2.8 Brownian Movement and Kinetic Theory of Gases

When a solid particle is suspended in a gas, gas molecules collide with it. If the particle is very large, the number of bombarding molecules on one side is almost equal to

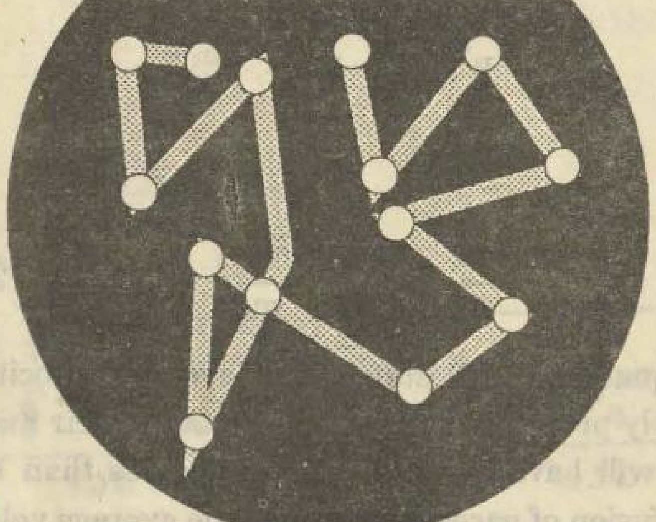


Fig. 2.14 — Brownian movement of a colloidal particle as seen through an ultramicroscope.

the number of bombarding molecules on the other side. If the size of particle is small, collisions of molecules on one side of the particle may be more than the other side. It causes the particle to move in a zigzag path. This zigzag motion is called Brownian movement. It is the direct evidence and supports the kinetic theory of gases.

2.9 Real Gases: The Non-Ideal Behaviour

When a gas obeys Boyle's Law and Charles's Law, it is said to be ideal. According to Boyle's Law

$$PV = K \text{ (at constant temperature)}$$

Charle's

The increase or decrease in pressure would result in proportionate decrease or increase in volume. Hence, if a graph is plotted between P on X-axis and PV on Y-axis, the result would be a horizontal line for an ideal gas at a definite temperature. This line should be parallel to pressure axis.

But all real gases have been found to show marked deviations from ideal behaviour especially at high pressures. The magnitude and nature of these deviations for H_2, CH_4 and CO and He at O °C are shown. When these gases are handled for some sort of experiment, at 100 °C, the deviations become less serious.

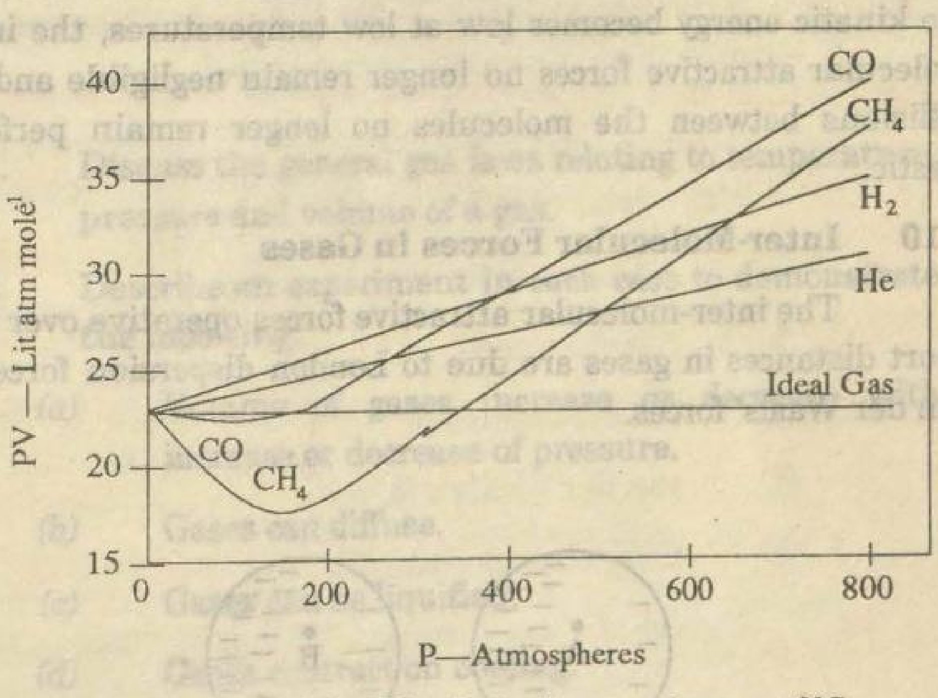


Fig. 2.15 : PV v. P plot for several gases at 0°C.

This graphical picture shows that gases behave non-ideally.

(i) At low temperature

(ii) At high pressure

The reason for this is that there are two ideal assumptions in the kinetic molecular theory of gases.

(i) The actual volume of a gas is negligible as compared to the volume occupied by the gas.

(ii) No forces of attraction or repulsion are present between the molecules and each molecule behaves independently.

The first postulate is responsible for the deviation at very high pressure and second postulate for the deviation at low temperatures. This is because at high pressure the gas molecules come closer. The empty space between the molecules decreases and as a result the volume occupied by the actual gas molecules does not remain negligible as compared to the total volume of the gas. The gas molecules do have attraction for each other. At high temperatures, the kinetic energy of the molecules is very large and the attractive forces become negligible. However when the kinetic energy becomes low at low temperatures, the inter-molecular attractive forces no longer remain negligible and the collisions between the molecules no longer remain perfectly elastic.

2.10 Inter-Molecular Forces in Gases

The inter-molecular attractive forces operative over very short distances in gases are due to London dispersion forces or van der Waals' forces.

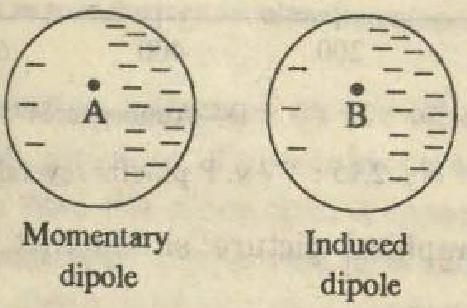


Fig. 2.16 — Vander waals forces (London Forces)

London forces present among all molecules of inert gases are generated due to temporary dipoles created because of rapid change in symmetry of the electron cloud of molecules. These forces are more effective at low temperatures and high

pressures. Let us see how these van der Waals' forces operate. Consider a monoatomic molecule of helium, He. Normally the negative charge is considered to be symmetrically distributed around the nucleus. Actually the electronic charge clouds around nuclei are rapidly oscillating. The oscillating electronic charge cloud may get slightly unsymmetrical producing a dipole. This momentary dipole induces a temporary dipole in the adjacent atom. As a result of it weak attractive forces between molecules are generated. Such forces are also called London forces.

EXERCISE

1. Discuss the general gas laws relating to temperature, pressure and volume of a gas.
2. Describe an experiment in each case to demonstrate the following:
   - *(a)* Volume of gases increase or decrease with increase or decrease of pressure.
   - *(b)* Gases can diffuse.
   - *(c)* Gases can be liquified.
   - *(d)* Gases contract on cooling.
3. Derive an expression for the general gas equation. On what factors does the value of universal gas constant depends?
4. Explain Dalton's law of partial pressure. Describe its important applications.
5. Explain absolute temperature on the basis of Charles' law.
6. State Graham's law of diffusion and describe an experiment to demonstrate it.

7. State and explain Avogrdro's law and Gay-Lussac's law of combining volumes. Give applications of Avogadro's law.

8. State basic postulates of kinetic molecular theory of gases and explain how gas laws can be derived from the kinetic molecular theory.

9. What is the difference between an ideal and a real gas? Why do the gases deviate from the ideal behaviour?

10. What will be the volume of 20 litres of a gas when it is compressed from 1 atmosphere to 200 atmospheric pressure at constant temperature?

(Ans: 0.1 litres)

11. Write detailed notes on the following:

(a) Absolute scale of temperature.

(b) Absolute zero.

(c) Elastic collisions.

(d) van der Waals's forces.

(e) Brownian movement.

12. A mass of a gas occupies 200 mL at 760mm Hg and 0°C. What volume will it occupy at 364K and at 1.5 atmospheric pressure?

(Ans: 177.7 mL)

13. Calculate the number of molecules in

(a) 1 litre of H_2 at STP.

(b) 2.0 litres of N_2 at STP.

(c) 2 litres of He at 27°C and 1 atm. pressure.

(d) 1050 mL of CO_2 at 25°C and 800mm Hg pressure.

(Ans: 0.27×10^{23} and 0.54×10^{23} molecules)

14. A sample of nitrogen gas, collected at 120 °C and 1.00 atmospheric pressure, has a volume of 380 mL. It is transferred to a 4 litre flask and cooled to 25 °C. What will be the pressure exerted by the gas at 25 °C?

(Ans: 54.72mm of Hg)

15. 60 litres of hydrogen gas were collected over water at 741 mm Hg pressure and at 23 °C. What volume would be the dry hydrogen occupy under standard conditions? The vapour pressure of water at 23 °C is 21.1 mm Hg.

(Ans: 52.43 mL)

16. A 12 litre flask at 30 °C contains a gaseous mixture of hydrogen and helium at a total pressur of 2.00 atmospheres. If 0.20 mole of helium is present, find out the partial pressure of each gas.

(Ans: P_H = 1.5867 atm, P_{He} = 0.4133 atm.)

17. A mixture of 50 g of hydrogen and 50g of helium has a total pressure of 1.5 atmospheres, What are the partial pressures of hydrogen and helium in the mixture in mm of Hg.

(Ans: PH_2 = 0.999 atm, PHe = 0.499 atm)

18. Air contains 78% of N_2, 21 % of O_2 and 1% of inert gases by volume. If the pressure of air is 760mm Hg, calculate the individual pressures of N_2, O_2 and inert gases.

Ans: PN_2 = 592.8 mm Hg.
PO_2 = 159.6 mm Hg.
P inert gases = 7.6 mm Hg

19. Calculate the molecular weight of a gas whose density at 40 °C and 785 mm Hg is 1.3 g/L.

(Ans: 32)

20. Calculate the density of methane at 25°C and one atmospheric pressure. The molecular weight of methane is 16.

(Ans: 0.654 g/L)

21. Equal volumes of HCl and SO_2 are present in a closed container. What would be the comparative rates of diffusion of these gases through the porous walls? The molecular weights of HCl and SO_2 are 36 and 64 respectively.

(Ans. HCl is 1.33 times faster than SO_2)

22. A 100 millilitre sample of hydrogen difuses through a porous container four times as rapidly as an unknown gas. Calculate the molecular weight of the unknown gas.

(Ans. 32 amu)

23. Fill in the blanks with suitable words, given in the brackets.

(i) Gasses ———— on heating and ———— on cooling. (contract/expand)

(ii) A ———— gas diffuses more rapidly than a ———— gas. (heavier/lighter)

(iii) The volume of given mass of gas varies ———— with the increase of pressure at constant temperature (inversly/directly).

(iv) Volume of given mass of a gas varies ———— with the increase of temperature at constant pressure. (directly/inversely)

(v) Volume of a given mass of a gas changes ———— as the pressure and ———— as the temperature. (directly/inversely)

(vi) The density of a gas varies ———— to pressure at given temperature (Inversely/directly)

(vii) The value of gas constant R is ———— J/K/mol. (0.0821/8.3143).

(viii) The value of gas constant ———— upon the nature of gas but ———— upon the units used. (depends/does not depend)

(ix) The number of H_2 and gases N_2 molecules are ———— in 0.01mL of both gases separately at S.T.P. (same/different)

(x) 1000 molecules of O_2 and N_2 at S.T.P. have ———— weights (same/different).

(xi) The collision of ideal gas molecules are ———— . (elastic/inelastic)

(xii) The velocity of H_2 molecules is ———— than O_2 molecules at 1 atm pressure and 0°C. (less/more/equal)

(xiii) ———— temperature and ———— pressure makes the gases non-ideal. (high/low)

(xiv) The non-ideality of a gas ———— upon the its nature. (depends/does not depend)

(xv) Generally—gases are more non-ideal than ———— gases. (non polar/polar)

(xvi) ———— pressure causes the forces of attractions among the molecules of a gas. (low/high)

(xvii) Van der waal's forces are ———— forces. (permanent/temporary)

(xviii) London forces are also called ———— forces. (Van der Waal/dipole induced/dipole)

(xix) Dalton's law is ———— when attractive forces are present among the gas molecules in a mixture of two gases. (obeyed/not obeyed)

(xx) The velocities of gas molecules in a mixture of gases are ———— at same temper-ature. (same/not same).

24. Explain the following with reasons:

(i) Lighter gases can diffuse more rapidly than heavier ones.

(ii) High pressure and low temperatures make the gases non-ideal.

(iii) H_2 and He are ideal at room temperature and ordinary pressure but SO_2 is non-ideal.

(iv) Regular air cannot be used in diver's tank.

(v) At high altitudes, the pilots have uncomfortable breathing.

(vi) $-273.16°C$ is the lowest possible temperature.

(vii) Different gases move with different velocities at the same temperature although their kinetic energies are same.

(viii) Intermolecular forces due to dipole—dipole interactions are stronger than London dispersion forces.

3

LIQUIDS AND SOLIDS

3.1 Kinetic Molecular Description of Liquids and Solids

According to the kinetic molecular theory two forms of matter, i.e. gases, and liquids are composed of rapidly moving particles. In gases these particles or molecules are widely separated from each other and are moving in all directions. We, however, know that all gases can be converted into liquids and solids by compression and cooling. In the last chapter we saw that the average kinetic energy of a collection of gas molecules decreases as the temperature is lowered. If a sample of gas is cooled and compressed sufficiently, inter-molecular attractions overcome the kinetic energies as the molecules approach each other. At this point condensation *(liquefaction or solidification)* occurs. In this process of condensation the particles come so close to each other that the empty spaces between them are

reduced to the minimum, and as a result, the liquids and solids become almost incompressible.

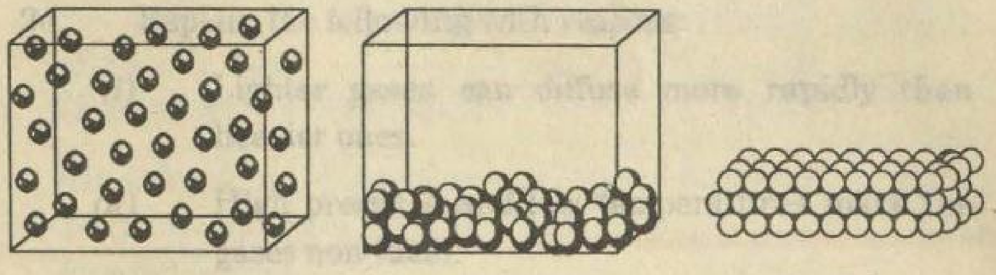


Fig. 3.1 — Kinetic molecular model of gas , liquid and solid.

In the liquid state, the forces of attraction among the particles are great enough to hold them together, yet not sufficient enough to stop all sort of translational motion as in case of solids. The particles of the liquid are able to slide past each other so that liquids assume the shape of the container. The liquids therefore, have definite volume but no definite shape. Like gases, liquids also diffuse into other liquids with which they are miscible. Solids on the other hand cannot ordinarily diffuse into other solids or mix to form homogeneous solutions like liquids and gases because the particles of solids possess only vibrational motion and no translational motion.

All liquids on further cooling are converted into solids. This is because cooling a liquid lowers its molecular kinetic energy until short range attractive forces overcome the decreasing kinetic energies of the molecules to cause crystallization. The temperatures at which gases are converted into liquids and the liquids into solids are characteristic of each substance.

The diffusion of a liquid is slow but takes place at a measurable rate. Diffusion occurs because molecules move from one place to another due to kinetic energy. In liquids, molecules do not move very far when they collide with neighbouring molecules. Repeated collisions with neighbouring and more

closely packed molecules hinder the migration of particles too far. Even while moving from one end of the container to the other liquid molecules meet billions of collisions among themselves. The ink and water diffuse slowly into each other to form a uniform diluted coloured solution.

3.2 Characteristic Properties of Liquids

The intermolecular forces in liquids and their molecular structure can be best understood by studying their physical properties such as vapour pressure, boiling point, surface tension and viscosity etc. Physical properties of liquids can be predicted for a known structure and vice versa. The physical properties of liquids can be classified broadly into three groups.

(i) **Colligative properties:** These properties depend mainly on the number of molecules and are independent of their nature. The lowering of vapour pressure, depression in freezing point, elevation of boiling point, osmotic pressure etc., are examples of such properties.

(ii) **Constitutive properties:** These properties depend mainly on the arrangement of atoms in the molecules and to a lesser extent on their number e.g., optical activity.

(iii) **Additive properties:** These properties are sum of the corresponding properties of individual components of system i.e., molecular weight, mass etc.

3.3 Intermolecular Forces and the Liquid State

In the last section we discussed phase changes—gas into liquid and liquid into solid, on the basis of the presence of intermolecular forces. The liquid properties such as boiling point, vapour pressure, surface tension, viscosity and heat of vaporization depend markedly on the strength of the intermolecular attractive forces. These forces are also directly related to the properties of solids such as melting point and the heat of fusion.

Intermolecular forces are forces that exist between individual particles (atoms, ions, molecules) of a substance. These forces are relatively weak as compared to *intramolecular forces, i.e.,* ionic and covalent bonds within a particle. For example consider the following two conversions:

(i) $H_2O(g) \longrightarrow 2H + O \quad \Delta H = +920kJ$

(ii) $H_2O(\ell) \longrightarrow H_2O(g) \quad \Delta H = +40.7kJ$

Conversion (i) indicates the dissociation or bond breaking of one mole of water molecules in gaseous state into hydrogen and oxygen atoms which requires 920 kJ of energy. Thus 920 kJ energy is required to break two O—H bonds. Conversion (ii) indicates the energy required to change one mole of water at 373 K(100°C) in liquid state to one mole of water molecules in gaseous phase at the same temperature which requires only 40.7 kJ. It is clear that the energy required in conversion (ii) represents the strength of inter-molecular forces which are much smaller than the covalent bonds that hold the hydrogen and oxygen atoms in the molecules. The strength of intermolecular forces determines whether a molecular substance is a gas, a liquid or a solid at that temperature.

There are three principal types of intermolecular forces:

(i) dipole-dipole forces,

(ii) hydrogen bonding,

(iii) London forces (or dispersion forces)

Together these forces are called *van der Waals' forces.* The stronger the van der Waals' forces, the higher the boiling points and heats (or enthalpies) of vaporization and fusion.

The dipole-dipole interactions are the inter-molecular forces that exist in polar molecules which attract each other electrostatically. The negative end of one molecule attracts the positive end of the other molecule. When a solid polar substance is heated the dipole-dipole forces must be overcome to break-up the crystal lattice and melt the substance. The strength of these

forces, along with others, therefore, affect the melting point and heats of vaporization.

Dipole-dipole forces persist in liquid state as well. The energy supplied to a liquid at its boiling point to convert it into vapours is used to overcome dipole-dipole forces and other intermolecular forces. The boiling points and heats of vaporization are, therefore, affected by the dipole-dipole interactions.

In general, the polar molecules in which dipole-dipole forces are operative have higher melting points, boiling points and heats of fusions and vaporization. A comparison of compounds with similar molecular masses, given below, illustrates the effect of dipole-dipole interaction on the properties of these substances.

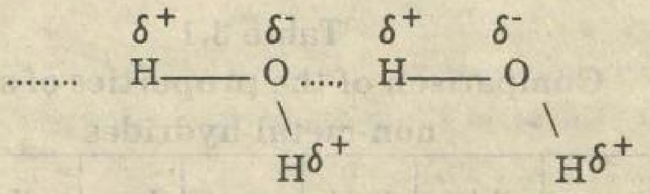
Table 3.1
Comparison of the properties of some non-metal hydrides

Hydride	Molar Mass (g/mole)	Dipole Moment (D)	m.p. (°C)	b.p. (°C)	Heat of Fusion at m.p. kJ/mole	Heat of Vaporization at b.p. kJ/mole
1. Silane (SiH_4) (non polar)	32.09	0	−185	−111	0.665	13
2. Phosphine PH_3 (Polar)	34.00	0.55	−134	−87.8	1.13	14.6
3. Hydrogen Chloride (HCl) (Polar)	36.46	1.04	−114	−84.9	1.99	16.1
4. Hydrogen Sulphide (H_2S) (Polar)	34.08	1.10	−85.86	−60.8	2.38	18.7
5. Water (H_2S) (Polar)	18.02	1.85	0.00	100	6.02	40.7

Look at the table 3.1. The first four hydrides have similar molecular weights. SiH_4 which is non polar (dipole moment = 0) has the lowest melting point, boiling point, heats

of fusion and vaporization. Hydrogen sulphide H_2S which has a dipole moment twice as much as phosphine (PH_3) has the higher b.p., m.p., heats of fusion and vaporization.

The dramatic deviations of water (H_2O) from the systematic trends shown by SiH_4, PH_3, HCl and H_2S indicate the presence of yet another type of much stronger intermolecular force in water. This special type of intermolecular force present in water is known as *hydrogen bonding.* A hydrogen bond is formed when a hydrogen atom bonded to a strongly electronegative atom, also interacts with the lone electron pair of a second electronegative atom near by. In water this interaction can be represented as under



The dotted line indicates a hydrogen bond.

Hydrogen bonds are not really chemical bonds in the formal sense. They are special, very strong case of dipole—dipole interactions. Hydrogen bonding occurs among polar covalent molecules containing H and one of the small, highly electronegative elements such as F, O or N.

As already discussed in section 2.9, the third type of intermolecular forces that are important at extremely short distances are known as *London forces or dispersion forces.* These forces exist in all types of molecules in condensed phases. They are the only intermolecular forces present among symmetrical non-polar substances such as CH_4, SO_3, CO_2, O_2,

H_2 and monoatomic noble gases. London forces result from the attraction of the positively charged nucleus of one atom for the electron cloud of an atom in nearby molecules. This induces temporary dipoles in the atoms or molecules. These forces are also, therefore, known as *dipole-induced dipole forces.* All these types of intermolecular forces are shown diagrammatically in Fig. 3.2.

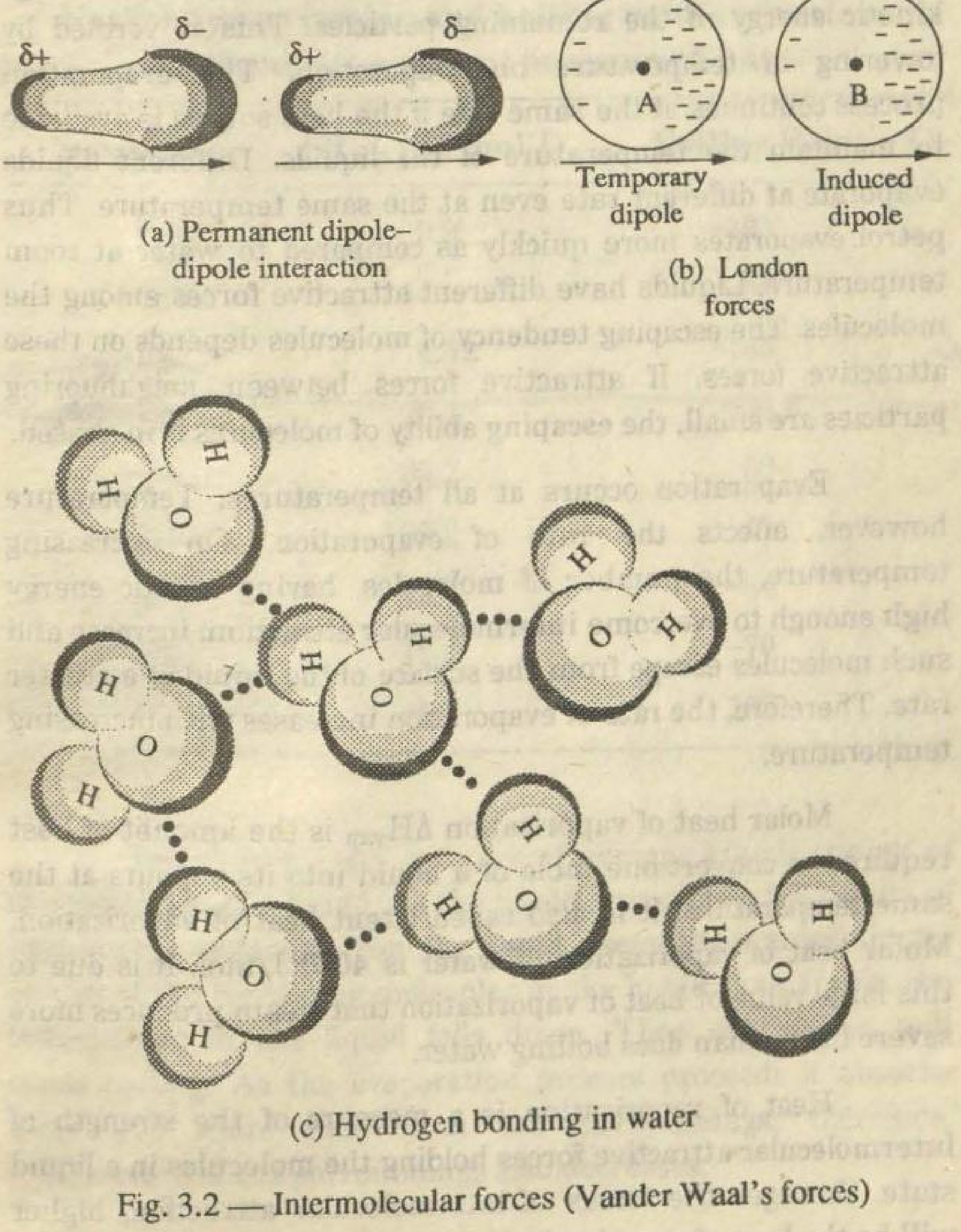


Fig. 3.2 — Intermolecular forces (Vander Waal's forces)

3.4 Evaporation

Liquids evaporate because of the escape of molecules from the surface of liquids. There are attractive forces among molecules which hold them together. The molecules with kinetic energy great enough to overcome the attractive forces can escape into the gas phase. The molecules with greater kinetic energy leave the liquid more quickly and cause a decrease in average kinetic energy of the remaining particles. This is verified by lowering in temperature on evaporation. The evaporation process continues at the same rate if the heat source is available to maintain the temperature of the liquids. Different liquids evaporate at different rate even at the same temperature. Thus petrol evaporates more quickly as compared to water at room temperature. Liquids have different attractive forces among the molecules. The escaping tendency of molecules depends on these attractive forces. If attractive forces between neighbuoring particles are small, the escaping ability of molecules is increased.

Evaporation occurs at all temperatures. Temperature however, affects the rate of evaporation. On increasing temperature, the number of molecules, having kinetic energy high enough to overcome intermolecular attraction, increase and such molecules escape from the surface of the liquid at a greater rate. Therefore, the rate of evaporation increases with increasing temperature.

Molar heat of vaporization ΔH_{vap} is the amount of heat required to convert one mole of a liquid into its vapours at the same temperature. It is also called latent heat of vaporization. Molar heat of vaporization of water is 40.7kJ/mol. It is due to this large value of heat of vaporization that steam produces more severe burns than does boiling water.

Heat of vaporization is a measure of the strength of intermolecular attractive forces holding the molecules in a liquid state. Stronger the forces of intermolecular attraction, higher will be the heat of vaporization.

Heat of vaporization increases in presence of hydrogen bonding because more energy will be required to overcome the forces due to hydrogen bonding. For example, the heat of vaporization of water which contains hydrogen bonds is higher than that of methane. The amount of heat required to vaporize one mole of liquid at its boiling point without change in temperature is called molar heat of vaporization.

Table 3.2

Heats of vaporization and boiling points of various substance at constant pressure of 1 atm

Substance	ΔH_{vap} (kJ mol^{-1})	Boiling Point (°C)
CH_4	9.2	−161
C_2H_6	14	−89
F_2	6.52	−188
Cl_2	20.4	−34.6
Br_2	30.7	59
HF	30.2	17
HCl	15.1	−84
HBr	16.3	−70
H_2O	40.7	100

Temperature is a measure of average kinetic energy of the molecules of a liquid. As the liquid evaporates, the escape of high energy molecules from the liquid lowers the average kinetic energy of the remaining molecules in the liquid. As a result, the temperature of the liquid falls down. Thus evaporation will cause cooling. As the evaporation process proceeds it absorbs more and more heat from the surroundings, therefore, temperature of the surroundings also decreases.

3.5 Vapour Pressure — An example of Dynamic Equilibrium

Whenever a liquid is placed in a close vessel, molecules leave the liquid phase and enter the gaseous phase. With the increase in number of molecules in the gaseous phase they collide with the molecules on the liquid surface and return to it. After some time the rates at which the molecules leave and return to the liquid phase become equal and equilibrium is established in the system (Fig 3.3)

$$\text{Vapour} \xrightleftharpoons{\text{at equilibrium}} \text{Liquid}$$

O——► Molecules undergoing vaporization

O—► Molecules undergoing condensation

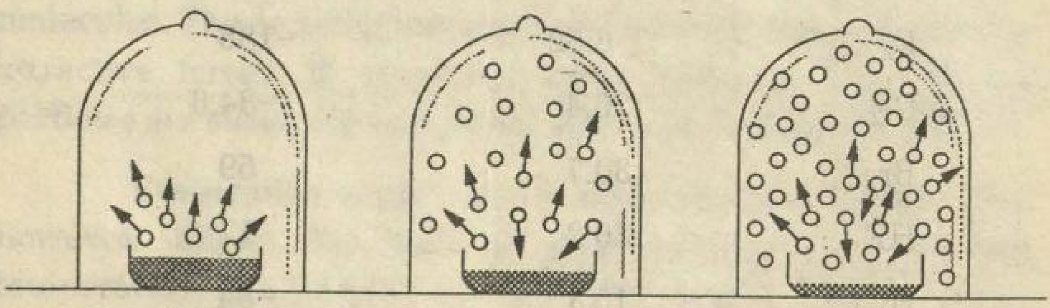


Fig. 3.3 (a) (b) (c)

(a) – A liquid is a allowed to evaporate into a closed vapor volume. Initially only vaporization occurs.

(b) – Condensation begins. However, because molecules are evaporating at a faster rate than they are condensing, the number of molecules in the vapor state continueus to increase.

(c) – The rate of condensation has become equal to the rate of vaporizaiton. Dynamic equilibrium is established. The number of molecules present in the vapor state remains constant over time, as does the pressure exerted by the vapor.

The molecules in the vapour phase exert a pressure in a similar manner as a gas would do. This pressure of vapours in equilibrium with its liquid phase is called vapour pressure of the liquid. The pressure exerted by the vapours in equilibrium with its pure liquid at a given temperature is called the vapour pressure of the liquid. The vapour pressure is a measurable

quantity. A mercury barometer can be used to measure vapour pressure.

If a drop of a liquid is placed beneath the dish of mercury, with the help of a dropper, the liquid drop will rise above mercury column because most liquids are less dense than mercury, and on reaching above the surface of mercury a part of liquid will evaporate and the resultant vapour will push the mercury column downward with decrease in length of the column. The decrease in length of mercury will be equal to the vapour pressure of the liquid (Fig. 3.4).

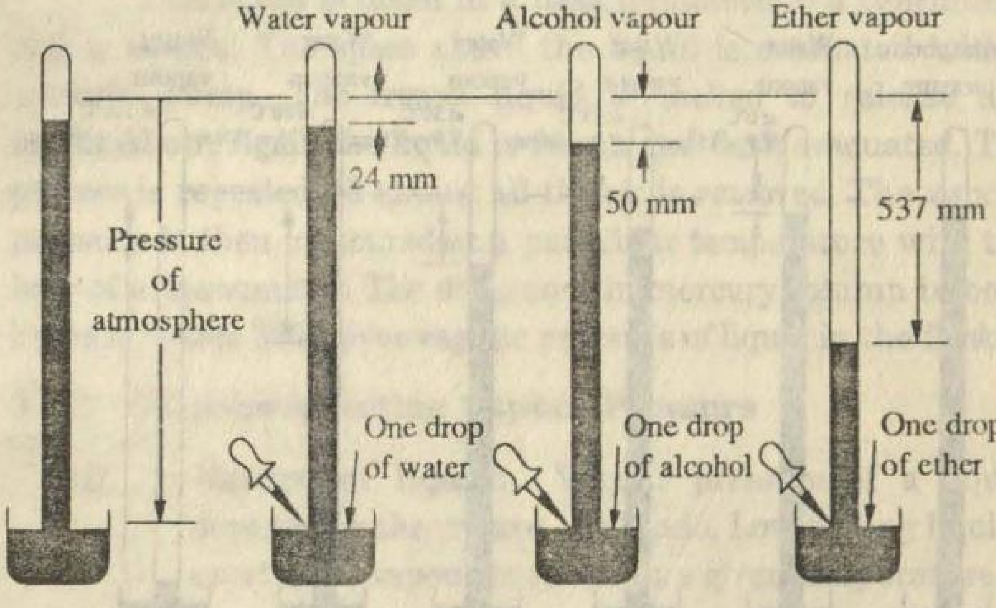


Fig. 3.4 — Vapour pressure of water (H_2O), ethyl alcohol (C_2H_5OH) and diethyl ether ($C_2H_5OC_2H_5$) at 25°C and at 760 mm Hg pressure

This experiment can be performed at various temperatures. The vapour pressure of a liquid increases with temperature. Table 3.3 lists the vapour pressure of some liquids at different temperatures.

Table 3.3

Vapour Pressures (in mm of Hg)

Temp(°C)	Water	Ethyl alcohol	Ether
0	5	12	185
20	18	43	442
40	55	132	920
60	149	347	1730
80	355	814	3000
100	760	1780	4865
120	1489	3535	7495

The vapour pressure of water increases with temperature and becomes equal to 760 mm at the boiling point (Fig. 3.5)

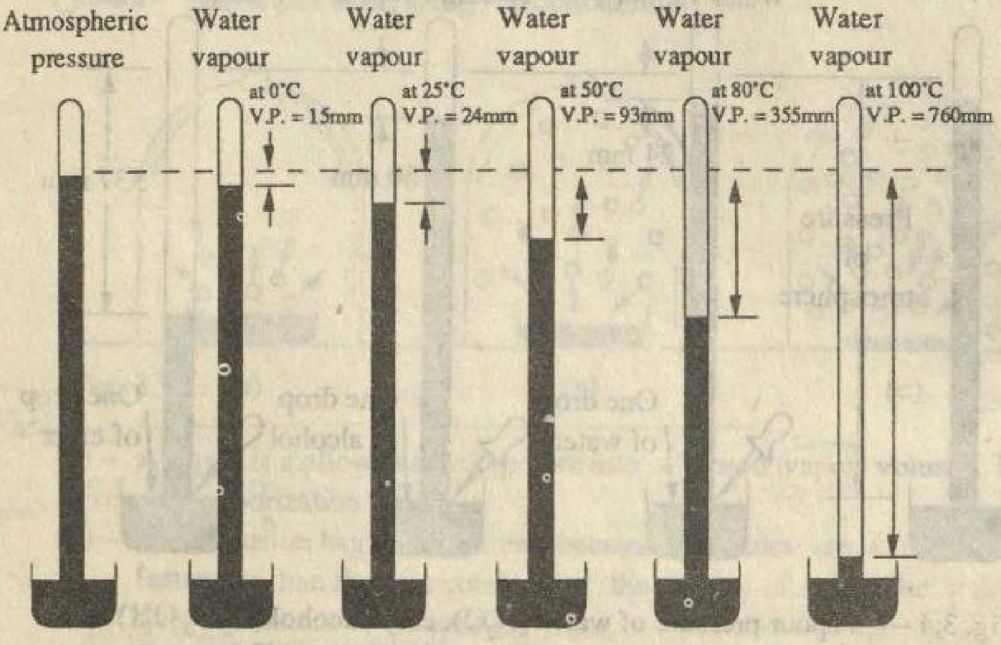


Fig. 3.5 — Effect of temperature on vapour pressure of water

3.5.1 Measurement of Vapour Pressure

For accurate determination of vapour pressure of a liquid at a particular temperature, the following apparatus is used under vacuum (Fig. 3.6)

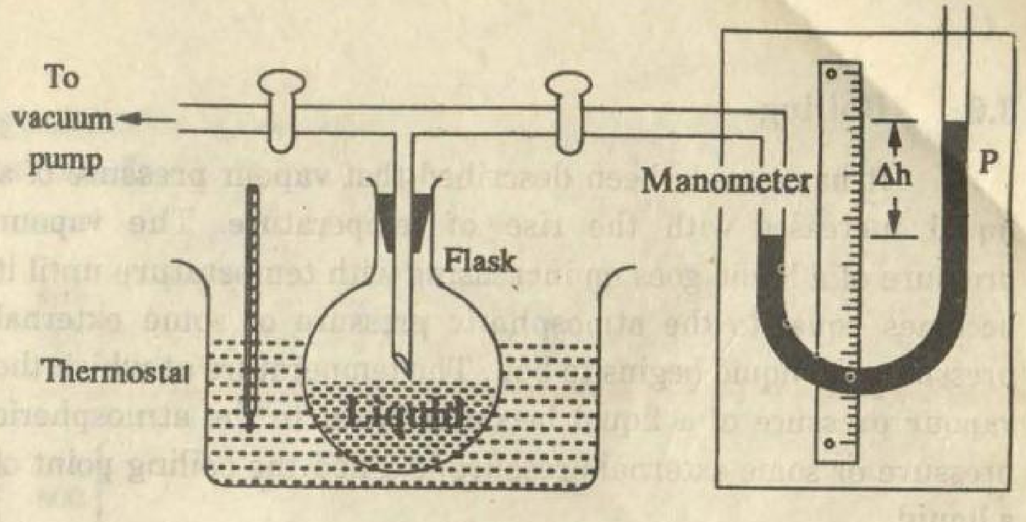


Fig. 3.6 — Accurate measurement of vapour pressure of a liquid.

$$V.P = P_{atm} + \Delta h$$

The liquid is taken in a flask immersed in a thermostat and is frozen. The space above the liquid is evacuated with a vacuum pump. The frozen liquid is melted to release any entraped air. Again the liquid is frozen and flask evacuated. The process is repeated till almost all the air is removed. The vapour pressure is then measured at a particular temperature with the help of a manometer. The difference in mercury column in both limbs is noted. This gives vapour pressure of liquid in the flask.

3.5.2 Factors Affecting Vapour Pressure

(i) **Nature of liquid:** Vapour pressure of a liquid depends on the nature of a liquid. Low boiling liquids exert more vapour pressure at a given temperature.

(ii) **Intermolecular Forces:** Vapour Pressure of a liquid depends on the extent of intermolecular forces. Stronger the intermolecular forces, lower is the vapour pressure of the liquid. Liquids with less intermolecular forces have high vapour pressures at a given temperature and are more volatile.

(iii) **Temperature:** The vapour pressure of a liquid increases with increase of temperature. This is because the average kinetic energy of the molecules increases with temperature, which causes increase in vapour pressure.

The vapour pressure of a liquid is independent of the amount of liquid.

3.6 Boiling

It has already been described that vapour pressure of a liquid increases with the rise of temperature. The vapour pressure of a liquid goes on increasing with temperature until it becomes equal to the atmospheric pressure or some external pressure and liquid begins to boil. The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure or some external pressure is called the boiling point of a liquid.

At boiling point, the vapour pressure of the liquid is so high that it pushes the atmosphere aside.

The boiling point of a liquid remains constant even though heat is continuously supplied to the liquid at its boiling point. Instead of raising the temperature of the liquid, the absorbed energy is now used to overcome the forces of attraction to separate liquid molecules and to convert liquid at its boiling point to a gas and is called the latent heat of vaporization. Latent heat of vaporization of water is 40.7 kJ mol^{-1}. The same amount of heat must be released when water vapours condense back to water at 100°C and is called heat of condensation. If atmospheric pressure is less than one atmosphere (760 mm of Hg) the boiling point decreases. Boiling point decreases because vapour pressure becomes rather readily equal to lower atmospheric pressure at lower temperatures. Thus water boils at temperatures lower than 100°C at higher altitudes. So water would boil at about 98°C at Murree hills (P = 0.921 atm) because atmospheric pressure is lower over there. Cooking times are therefore longer at that place than plain areas of Pakistan.

If external pressure is increased, the boiling point of water can be raised. This process is carried out in a pressure cooker which is a closed container. Vapours are not allowed to escape. They, therefore, develop more vapour pressure in the cooker and boiling point of water increases. Thus pressure cooker helps in cooking the meat and vegetables quickly even at

high altitudes. The vapour pressure-boiling point relationship is shown in Fig. 3.7

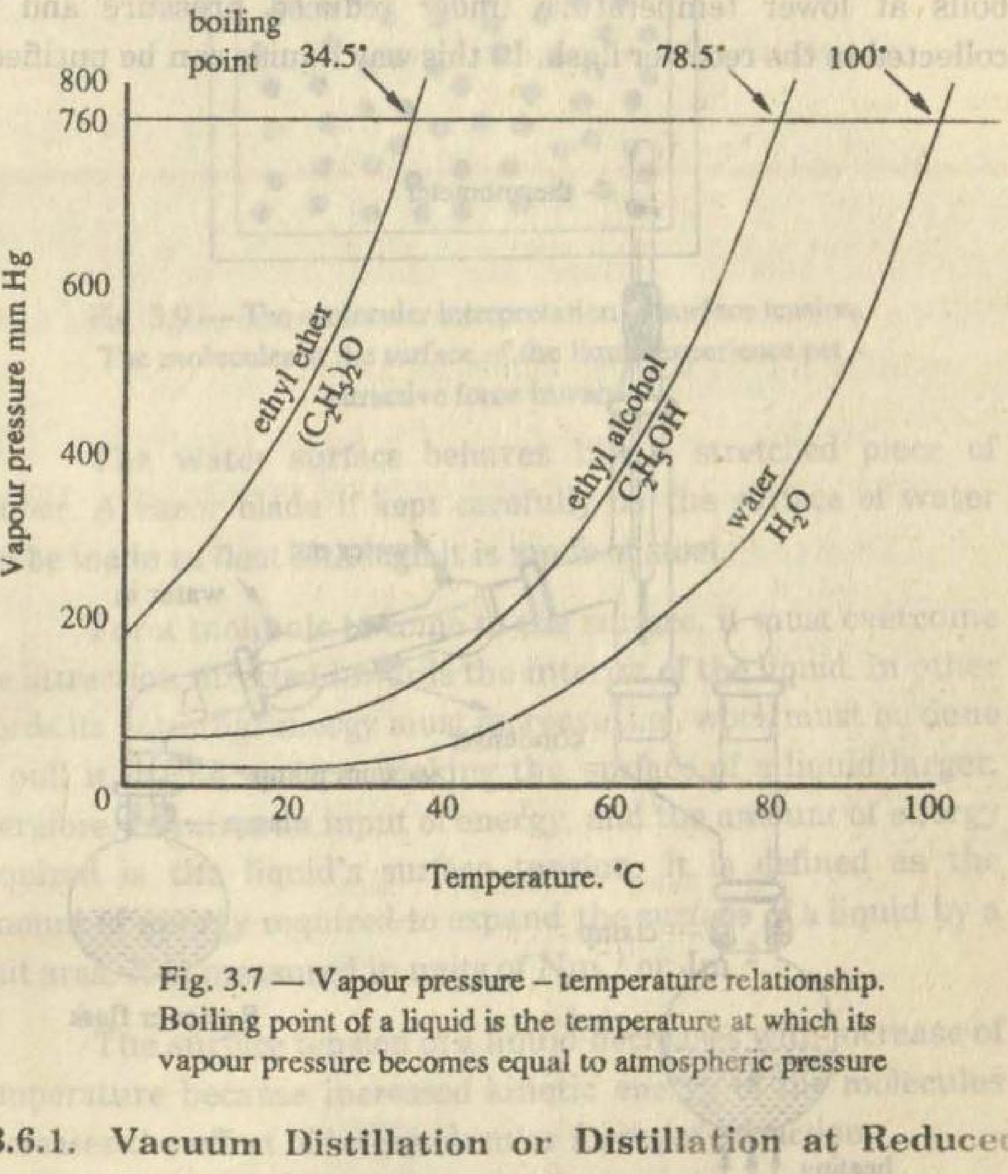


Fig. 3.7 — Vapour pressure – temperature relationship. Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to atmospheric pressure

3.6.1. Vacuum Distillation or Distillation at Reduced Pressure

Vacuum distillation is based on the principle that boiling points are lowered at lower vapour pressures. Some liquids with high boiling point can decompose if distilled. In order to boil or distil them at lower temperature, pressure is lowered or distillation is carried out under vacuum. Glycerine boils at 290°C under normal atmospheric pressure (760 mm Hg) but on lowering pressure to 50 mm Hg it can be distilled at 210°C.

A simple vacuum distillation apparatus is shown in Fig 3.8. It consists of boiling flask connected to a receiver flask

through a condenser. The tube near receiver flask is connected to a vacuum pump to reduce the pressure. On heating, liquid boils at lower temperature under reduced pressure and is collected in the receiver flask. In this way liquids can be purified.

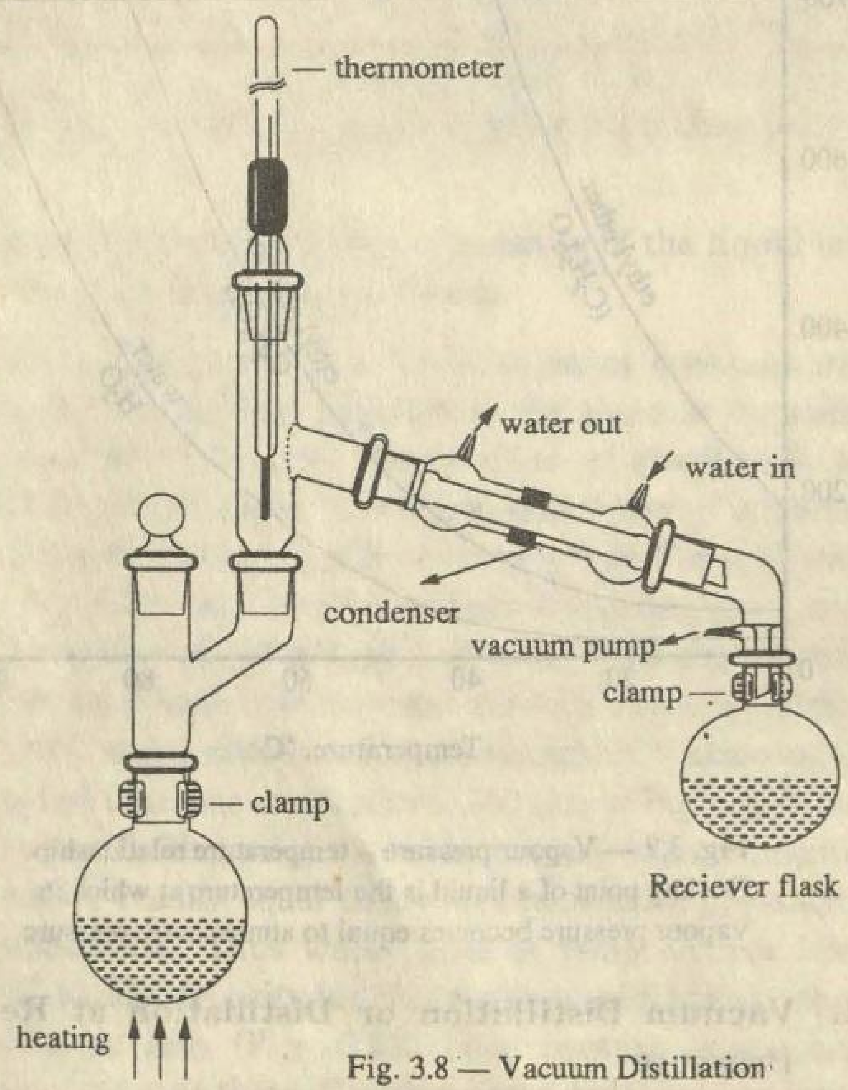


Fig. 3.8 — Vacuum Distillation

3.7. Surface Tension

Liquid molecules have the property of cohesion. Cohesion is the tendency of a liquid to cling together. Cohesive forces between water molecules are due to hydrogen bonding. The molecules at the surface of water are attracted by many molecules below it but not from above. The molecules at the surface, therefore feel a net attraction inward. This attraction creates surface tension. (Fig. 3.9).

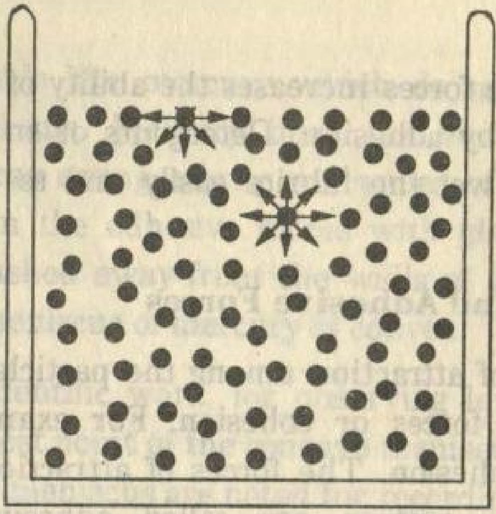


Fig. 3.9 — The molecular interpretation of surface tension. The molecules at the surface of the liquid experience net attractive force inward.

The water surface behaves like a stretched piece of rubber. A razor blade if kept carefully on the surface of water can be made to float although it is made of steel.

For a molecule to come to the surface, it must overcome the attraction directed towards the interior of the liquid. In other words its potential energy must increase, i.e., work must be done to pull it to the surface. Making the surface of a liquid larger, therefore, requires an input of energy, and the amount of energy required is the liquid's surface tension. It is defined as the amount of energy required to expand the surface of a liquid by a unit area. It is measured in units of Nm^{-1} or Jm^{-2}.

The surface tension of a liquid decreases with increase of temperature because increased kinetic energy of the molecules decreases the effect of intermolecular forces of attraction.

Water has high surface tension because of hydrogen bonding. Rain drops have spherical shape because a sphere has the least surface to volume ratio which it acquires due to surface tension. Other liquids also show the same tendency.

Detergents reduce the surface tension of water by breaking up the hydrogen bonding. The cohesive forces between water molecules are reduced by these substances called surfactants (surface-active agents) or wetting agents. The

reduction of cohesive forces increases the ability of the liquid to wet a solid surface by adhesion. Detergents or surfactants are used in laundry to wet the fabrics easily and to remove dust particles.

3.7.1 Cohesive and Adhesive Forces

The forces of attraction among the particles of a liquid are called cohesive forces or cohesion. For example, surface tension is due to cohesion. The forces of attraction between a liquid and another surface are called adhesive forces or adhesion. For example, attraction between water molecules and the particles of glass is called adhesion.

The shape of the surface of a liquid in a cylindrical container is called meniscus. It may be either concave or convex.

Liquids like water which wet glass form a concave meniscus. This is due to strong interactions between liquid such as water and the surface of the glass. Thus a liquid with stronger adhesive forces than cohesive forces shows concave meniscus. These liquids have tendency to climb up the walls of the vessel and increase the surface area of contact with the vessel. (Fig. 3.10)

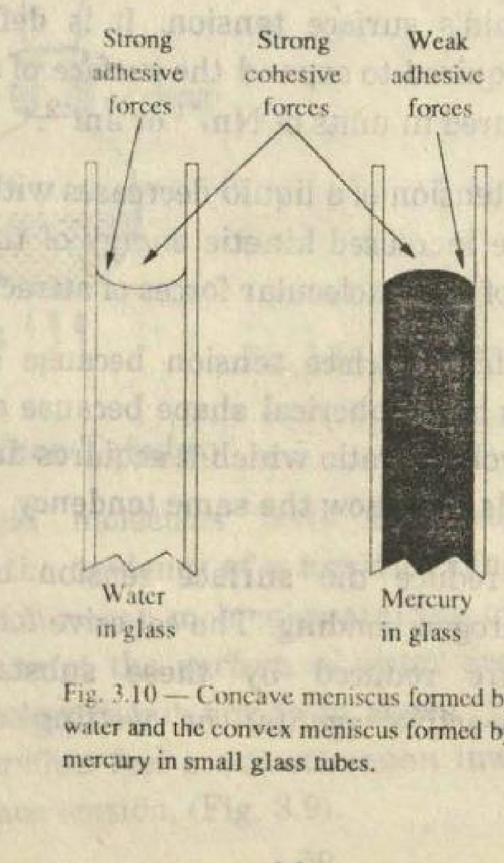


Fig. 3.10 — Concave meniscus formed by water and the convex meniscus formed by mercury in small glass tubes.

Liquids like mercury which do not wet glass form a convex meniscus. Mercury does not wet glass because the cohesive forces acting among molecules of mercury are much stronger than the adhesive forces with glass. The mercury is therefore, pushed away from the walls of glass at the point of contact. So meniscus of mercury is convex.

In scientific work, for observing level of a liquid in a tube, the lowest point of the concave meniscus and highest point of the convex meniscus are noted for recording the reading.

3.7.2 Capillary Action

The rise of a liquid in a small capillary tube is called capillary action.

The height of the liquid risen in the capillary tubes depends upon the diameter of tube. Tubes of narrower bores can show more height. The height of column is decided by compromise of upward deriving force and the downward gravitation pull (Fig. 3.11).

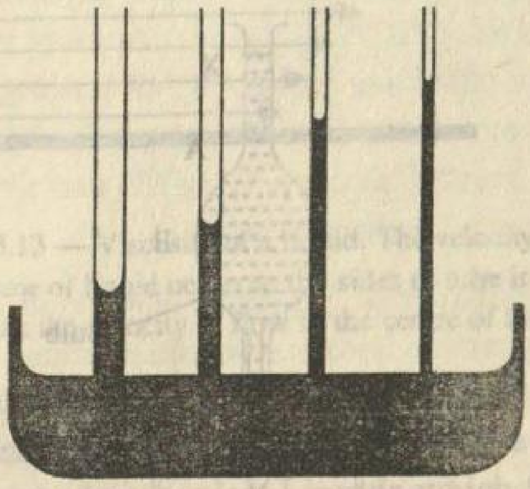


Fig. 3.11 — Capillary Action. Water rises higher in narrower capillaries.

Capillary action is due to strong adhesion of water molecules with surface of the tube. Cotton, paper and wicks

absorb water by capillary action. Water rises in narrow channels of these materials. It is the capillary action which causes rise of water from the soil to plants.

A drop of ink or water spreads on a blotting paper because of the capillary action of pores in the paper. Each pore acts as a small capillary tube.

3.7.3 Measurement of Surface Tension

There are several methods which are employed for measuring surface tension of a liquid. Some of them are:-

(i) The torsion method.

(ii) The capillary method.

(iii) The drop or stalagmometer method.

Drop weight method is commonly employed. Stalagmometer is used in this method. Stalagmometer consists of a glass bulb between tubes A and C, respectively (Fig. 3.12).

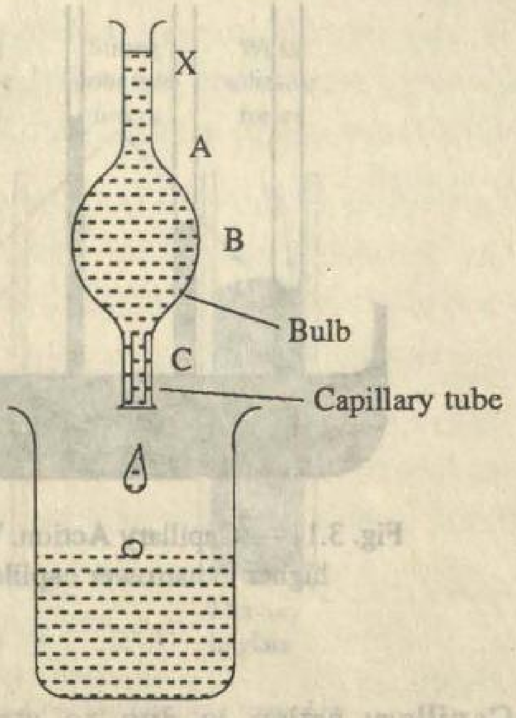


Fig. 3.12 — Stalagmometer

Liquid is filled in the dry clean stalagmometer upto 'x' with the help of suction and then it is allowed to flow down slowly in the form of drops. The number of drops formed with water and the number of drops formed with the same volume of another liquid are counted. Surface tension is calculated on the basis of the following equation:

$$\gamma_l = \frac{n_w\, d_l}{n_l\, d_w} \times \gamma_w \text{ .... (3.1)}$$

Where γ_l, d_l and n_l are surface tension, density and number of drops of given liquid and γ_w, d_w and n_w are the corresponding values for water.

3.8 Viscosity

Liquids have the ability to flow because molecules of the liquid can slide over each other. The resistance of a liquid to its flow is called viscosity (Figure 3.13). In other words, viscosity of a liquid is a measure of its internal resistance to flow.

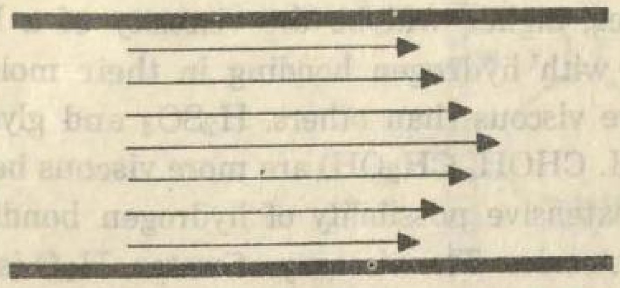


Fig. 3.13 — Viscosity of a liquid. The velocity of flow of liquid nearer to the sides of tube is less than the velocity of flow in the centre of tube.

The resistance to flow is because of the internal friction among the layers of molecules. Liquids which flow very slowly like honey or glycerine, have high viscosities as compared to ether and water having low viscosities.

with ring shaped S_8 molecules is less viscous than long chain tangled S_n molecules at 190°C. Therefore, liquids with irregular molecular shapes are more viscous i.e., honey.

(v) **Density:** Greater the density more will be the viscosity of a liquid and vice versa.

3.8.2 Measurement of Viscosity

It is not easy to measure absolute value of viscosity of a liquid. Therefore, relative viscosity of a liquid is determined.

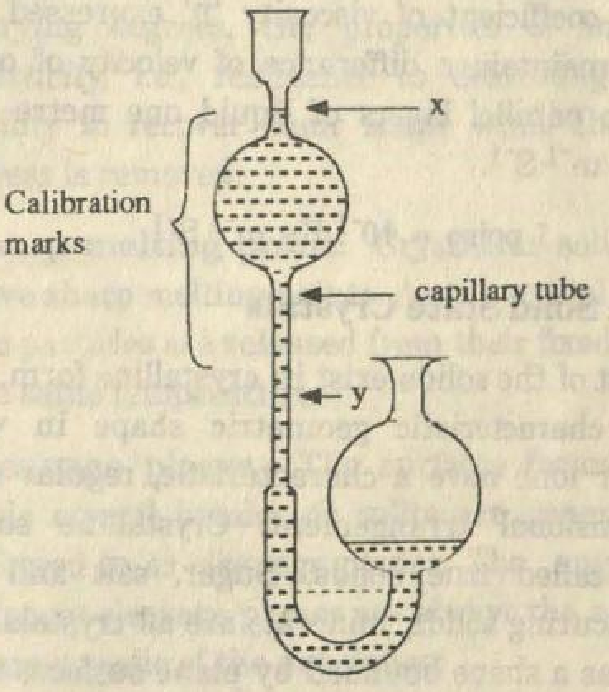


Fig. 3.14 — Ostwald's Viscometer

Ostwald's viscometer (Fig. 3.14) is used to measure the relative viscosity of a liquid. It consists of a capillary tube connected at its upper end with a bulb 'b'. Two marks 'x' and 'y' are etched on the viscometer and the liquid under test is allowed

to flow between marks 'x' and 'y'. The time of flow is noted. Viscometer is now cleaned and water is added in it. Time is again noted for water to flow between marks 'x' and 'y'. Relative viscosity of liquid is calculated from the formula,

$$\frac{\eta_l}{\eta_w} = \frac{d_l t_l}{d_w t_w} \quad \text{.................} \quad (3.2)$$

Where η_l, d_l, t_l and η_w, d_w, t_w are viscosities, densities and time of flow of a liquid and water, respectively.

The relative viscosity is defined as the ratio of viscosity of a liquid to the viscosity of water taken as standard. The viscosity of water is taken as 1 centipoise at 25°C.

The coefficient of viscosity 'η' expressed as the force required to maintain a difference of velocity of one metre/sec between two parallel layers of liquid one metre apart. Its S.I units are $Kg\ m^{-1}\ S^{-1}$.

$$1 \text{ poise} = 10^{-1}\ Kg\ m^{-1}\ S^{-1}$$

3.9 The Solid State Crystals

Most of the solids exist in crystalline form. A crystal is a solid with characteristic geometric shape in which atoms, molecules or ions have a characteristic, regular and repetitive three dimensional arrangement. Crystalline solids are also sometimes called true solids. Sugar, salt and most of the naturally occuring solids, minerals are all crystals. A crystal is a solid that has a shape bounded by plane surfaces intersecting at fixed angles.

3.10 Characteristics of Crystals

Several characteristics of crystals distinguish them from gases and liquids.

(i) **Definite shape and volume:** Crystals retain their shapes under small shear stresses of gravity, whereas, gases expand to fill any available volume

and liquids assume the shapes of the vessels that contain them.

(ii) **Anisotropy:** Gases and liquids exhibit properties that are independent of direction (i.e., they are *isotropic*), while crystals in general, because of their internal order, may have certain physical properties that vary with direction (i.e., they can be *anisotropic*). For example electrical conductivity or refractive index may be greater in one direction than another.

(iii) **Hardness and Elasticity:** Crystals possess, in varying degrees, the properties of *hardness and elasticity*, i.e., resistance to deforming forces and ability to recover their shape when the deforming stress is removed.

(iv) **Sharp melting point:** Crystalline solids generally have sharp melting points. As the crystal is heated all the particles are released from their fixed positions at the same temperature.

(v) **Cleavage plane:** The surfaces formed when an ionic crystal breaks or splits are generally planes- referred to as *cleavage planes.* The angles between adjacent cleavage planes are always the same and are characteristic of the substance.

3.11 Appearance of Crystals

Crystals are usually prepared (or grown) by slow cooling of a substance in liquid state or by cooling of a saturated solution. The outer appearance or shape of the crystal depends on how it is prepared and under what conditions. For example a substance with a cubic crystal structure may develop into a cube, a flat plate or a long needle like structure. Fig. 3.15 shows the growth of a cubic crystal in three different forms. The shape in which a crystal usually grows is called its habit. Sodium chloride has a cubic habit.

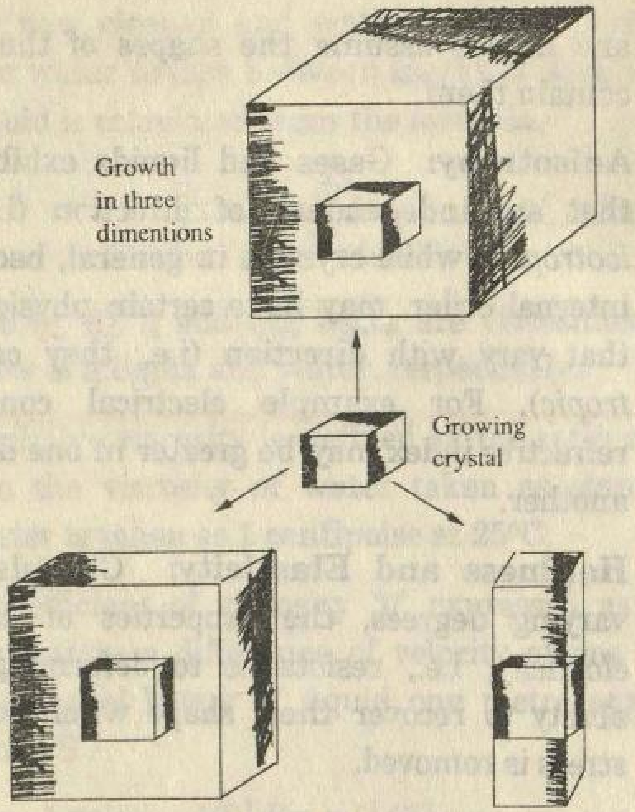


Fig. 3.15 — Growth of crystal in three shapes in a cubic system.

3.12 Isomorphism and Polymorphism

Two substances that have the same crystal structure are said to be *isomorphous.* The formulae of isomorphous substances usually reveal that their atoms are in the same ratios. For example study the formulae of the following isomorphous substances:

Isomorphs	atomic ratio	Crystal structure
NaF and MgO	1:1	Cubic
K_2SO_4 and K_2SeO_4	2:1:4	Orthorbombic
$NaNO_3$ and $CaCO_3$	1:1:3	Rbombohedral

Some isomorphous substances can crystallize together to give mixed crystals. The physical and chemical properties of isomorphs are quite different from one another.

A single substance that crystallizes in two or more different forms under different conditions is said to be *polymorphous*. The following substance exist in more than one crystalline forms:

Carbon, (graphite and diamond)

Sulphur, (rhombic and monoclinic)

Silica, (quartz, feldspars)

In case of elements, the polymorphic forms are called *allotropic* forms.

The temperature at which one crystalline form of a substance changes to another is called a *transition temperature*. For example the transition temperature of S_8 sulphur is 95.5°C.

$$\underset{\text{(rhombic)}}{S_8} \xrightleftharpoons{\text{above } 95.5^\circ C} \underset{\text{(monoclinic)}}{S_8}$$

The transition temperature is the temperature at which the two crystalline forms can coexist in equilibrium with each other. Other examples are as under.

$$\underset{\substack{\text{grey}\\\text{(orthorhombic)}}}{Sn} \xrightleftharpoons{18^\circ C} \underset{\substack{\text{white}\\\text{(tetragonal)}}}{Sn}$$

$$\underset{\text{(rhombohedral)}}{KNO_3} \xrightleftharpoons{128.5^\circ C} \underset{\text{(orthorhombic)}}{KNO_3}$$

3.13 Unit Cell and the Crystalline Lattice

All crystals contain regularly repeating arrays of atoms, molecules or ions. To describe such a repeating pattern we must specify two things *(i)* the size and shape of repeating unit and *(ii)*

the contents of the unit. In a crystal the repeating unit is three dimensional and its contents consist of atoms, molecules and ions. The smallest unit of volume of a crystal showing all the characteristics of its pattern is a *unit cell.*

The unit cell is described by the length of its edges a, b, c which are related to the spacing between layers and the angles α, β, γ between the edges

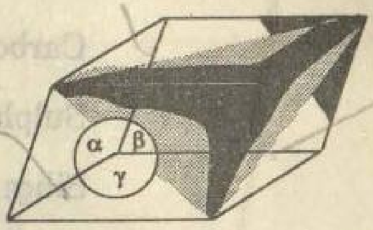


Fig. 3.16 — Representation of a unit cell

A simple three dimensional unit cell is shown in Fig. 3.16

In order to avoid dealing with repeat units of a crystal all the time, we may replace each repeat unit in the crystal by a point placed at the same place in the unit. All such points would then have the same environment and indistinguishable from each other.

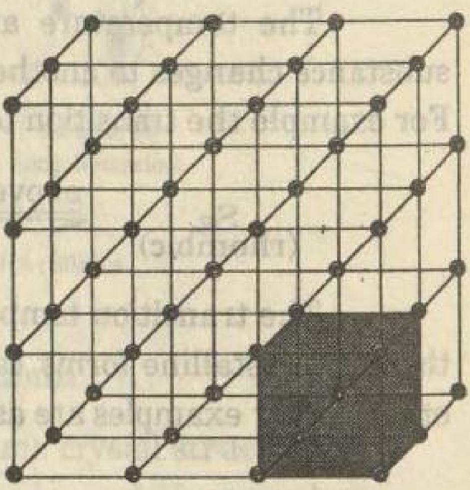

Simple cubic lattice

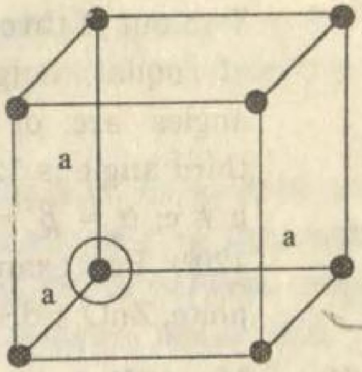
Fig. 3.17 — Crystal Lattice with a unit cell (shaded portion)

The resulting three dimensional array of points is called a *crystal lattice or space lattice*. A simple cubic space lattice with a unit cell is shown in Fig. 3.17.

3.14 The Crystal Systems

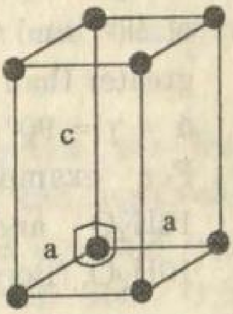
Different types of crystals have been identified. The individual crystals are identified by the lengths of the unit cells and the corresponding angles between them. Seven crystal systems have been identified Fig. 3.18 (a – g).

(i) **Cubic System:** In cubic system all the three axes are of equal length and at right angles to each other. (a = b = c; $\alpha = \beta = \gamma = 90^o$). Examples are crystals of NaCl, NaBr, diamond etc.



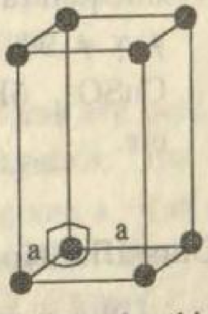
(a) Cubic

(ii) **Tetragonal system:** Two out of three axes are of equal length but all are at right angles to each other. (a = b ≠ c; $\alpha = \beta = \gamma = 90^o$). For example, SnO_2, $BaSO_4.4H_2O$ etc.



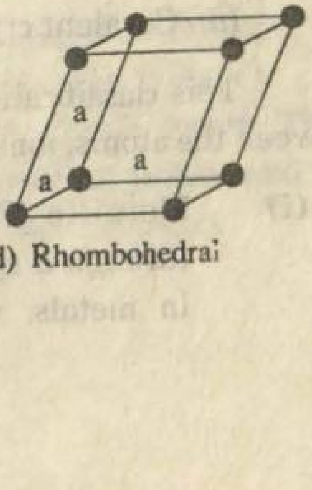
(b) Tetragonal

(iii) **Orthorhombic system:** All the axes are unequal and at right to each other (a≠ b ≠ c; $\alpha=\beta=\gamma=90^o$). For example $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$ etc.



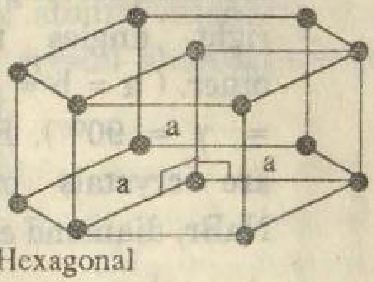
(c) Orthorhombic

(iv) **Trigonal or Rhombohedral system:** In this system all axes intersect at equal angles but at an angle of more than 90° and less than 120°. (a = b = c; $\alpha = \beta = \gamma > 90^o$ and $<120^o$) For example, $NaNO_3$, KNO_3, etc.



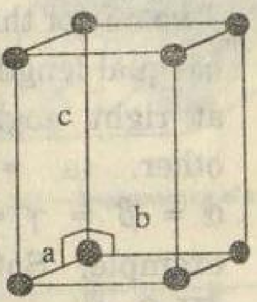
(d) Rhombohedral

(v) **Hexagonal system:** Two out of three axes are of equal length. Two angles are of 90° and third angle is 120°. ($a = b \neq c$; $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$) For example, graphite, ZnO, CdS etc.



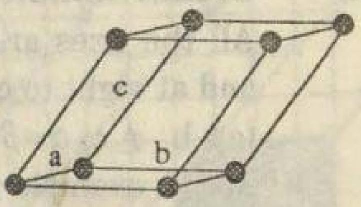
Hexagonal

(vi) **Monoclinic System:** All the three axes are unequal. Two angles are of 90° and the other is greater than 90° ($a \neq b \neq c$; $\alpha = \gamma = 90^\circ$ and $\beta > 90^\circ$) For example $Na_2CO_3.10H_2O$ and $Na_2B_4O_7.10H_2O$, (Borax) etc.



Monoclinic (f)

(vii) **Triclinic System:** All three axes and angles are unequal ($a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$) For example, $CuSO_4.5H_2O$, $K_2Cr_2O_7$ etc.



Triclinic (g)

Fig. 3.18

3.15 Classification of Crystals

Crystals can be classified in to four types:

(i) Metallic crystals *(ii)* Ionic crystals

(iii) Covalent crystals *(iv)* Molecular crystals.

This classification is based upon the nature of bonding between the atoms, ions or molecules in the solids.

(i) **Metallic Crystals:** Metal atoms join together through a special type of bond called metallic bond In metals, valence electrons are loosely held and

move freely. They create a kind of negatively charged atmosphere around the positively charged metal ion. Such an atmosphere of electrons is called electron sea or electron gas.

In metallic crystals, two types of forces exist which are responsible for the formation of the metallic bond. A force of attraction exists between electron sea and positive ions. Repulsive forces also exist between positively charged ions. The metal ions are held at a distance where attractive and repulsive forces balance each other's effect. Metallic crystals are good conductors of heat and electricity. They have lustrous surfaces.

(ii) **Ionic Crystals:** These crystals are formed by interaction between positively and negatively charged ions. Oppositely charged ions are held together by electrostatic forces of attraction. Ionic crystals are hard, have high melting points and conduct electricity in molten state or in the solution. An ionic bond exists between the ions in these crystals i.e. $Na^+ Cl^-$.

(iii) **Covalent Crystals:** When atoms are held through covalent bonds, covalent crystals are formed. Covalent bonds are fairly strong and a lot of energy is required to break these bonds. For example, 331kJ/mol of energy is required to break C—C bonds of diamond. Some of the examples of covalent crystals are, silicon, and germanium crystals.

(iv) **Molecular Crystals:** In molecular crystals, the molecules such as H_2O, I_2, N_2, O_2, NH_3, etc., are held together through van der Waal's forces. These crystals are soft, have low melting points and are usually non conductor of heat and electricity.

3.16 Lattice Energy of Ionic Crystals

Lattice energy is defined as the amount of energy released when gaseous ions of opposite charges combine to give one mole of a crystalline ionic compound. The energy in this case is assigned negative value.

It is also defined as work (or energy) required to separate the atoms, molecules or ions in a crystal to infinite distance. The sign of energy in this case is positive. (See also Chapter-6)

Lattice energies of some alkali metal halides are given in Table 3.3

Table 3.3

Lattice Energies of Some Alkali Metal Halides

Compound	Lattice Energy (kJ mol^{-1})
Li Cl	833
Li Br	783
Na Cl	766
Na Br	728
K Cl	690
K Br	665
K I	630

3.17 Amorphous Solids and Glasses

Crystals possess a high degree of spatial order among their constituent atoms, ions or molecules. There are certain solids which lack the characteristic properties of crystals. Such solids in which the atoms, molecules, or ions have a random or non-repetitive three- dimensional arrangements are termed as *amorphous solids,* or commonly called glasses. Naturally occuring gem stone, opal and volcanic glass (obsidian) are two of the very few substances found in earth's crust that are amorphous. Like crystals, they may have hardness and

elasticity, yet in many respects they are vastly different from crystals. For example they possess no sharp melting point (they melt over a range of temperature) or heat of fusion. On atomic scale they lack the specific structure of crystals. In this respect they resemble liquids more closely than crystals. Glass, tar and many solid polymers are also amorphous solids.

EXERCISE

(1) Define and explain the following terms, with examples:

(*a*) Vapour pressure

(*b*) Surface tension

(*c*) Viscosity

(2) What is the effect of rise in temperature on the following?

(*a*) Viscosity

(*b*) Vapour pressure

(*c*) Surface tension

(3) What do you understand by vapour pressure of a liquid? How is it experimentally determined?

(4) What is boiling point of a liquid? How is it dependent on the atmospheric pressure?

(5) (*a*) Define heat of vaporization.

(*b*) What is the difference between heat of vaporization and molar heat of vaporization?

(6) Describe a method for the determination of viscosity of a liquid. What are its units?.

(7) What is surface tension? Give its units. How is it experimentally determined?

(8) (a) Name the factors which affect the viscosity of the liquid.

(b) What are the units of surface tension and viscosity?

(9) Give reasons for the following facts:

(a) A falling drop of liquid is spherical.

(b) A drop of ink spreads on a blotting paper.

(c) Evaporation of a liquid is accelerated by heating.

(d) Evaporation of a liquid causes cooling.

(e) Temperature of a liquid remains constant during boiling although heat is being supplied continuously.

(f) A liquid boils at different temperatures at sea level and at mountains.

(g) Surface tension of water is higher than ether at the same temperature and pressure.

(h) Meniscus of certain liquids curves upwards while those of others curves downwards.

(i) Mercury does not wet the walls of the container.

(j) It is easier to pour water than honey.

(k) Steam produces more severe burns than does the boiling water.

(10) Explain, on molecular level, why the temperature remains constant as heat is added to vaporize a liquid at its boiling point.

(11) What are London forces? What is their role in liquefaction of gases?

(12) What type (or types) of intermolecular attractive forces are found in the following:

(a) HBr *(b)* Kr *(c)* CH_4

(d) HF *(e)* CO_2 *(f)* NH_3

(h) SO_3

(13) If you were asked to compare the strengths of the intermolecular force in liquid A with those in liquid B, what type of data would you collect?

(14) What are hydrogen bonds? Why are they most important in compounds containing N—H, O—H and F—H bonds.

(15) Arrange the following in order of increasing strength of individual interactions for typical cases: hydrogen bonds, covalent bonds, London forces, permanent dipole-dipole interactions that do not belong to hydrogen bond.

(16) What are solids? Discuss their general characteristics.

(17) Classify crystals on the basis of different types of bonds and discuss the forces of bonding in each case.

(18) Describe various types of crystal systems.

(19) Discuss metallic, ionic, covalent and molecular crystals. Also give their characteristic properties.

(20) Draw diagrams for tetragonal, hexagonal, cubic and trigonal system of crystals. Explain the difference ir these systems giving one suitable example for each.

(21) Explain the following terms;

(a) Unit Cell

(b) Polymorphism

(c) Allotropy

(d) Amorphous solids

(e) Anisotropy

(f) Cleavage of crystals.

(g) Isomorphism.

(22) Define the following terms with suitable examples:

(a) Habit of a crystal

(b) Transition temperature

(c) Lattice energy

(d) Polymorphism

(23) Explain lattice and lattice energy.

(24) Explain the difference between isomorphism and polymorphism with examples.

(25) Fill in the blanks with suitable words given in the brackets.

(i) The unit of surface tension is ________ (poise/Nm^{-1})

(ii) The dimension of poise is ________ ($10^{-1}Kg\ m^{-1}s^{-1}$ $10^{3}kg\ m^{-1}s^{-1}$)

(iii) Water is ________ viscous than honey but ________ viscous than ether. (more/less)

(iv) Water produces ________ meniscus in air in capillary tube. (convex/concave)

(v) Mercury is a ________ liquid. (nonwetting/wetting)

(vi) The rising of a liquid in a capillary tube is due to ________. (viscosity/surface tension)

(vii) The structure of NaCl is ________ (hexagonal/cubic)

(viii) The atoms, molecules or ions in solids have ________ motion (translational/to and fro)

(ix) Evaporation and sublimation ________ one and same thing. (are/are not)

(x) Surface tension is ________ property but mass is ________ property (constitutive/additive/colligative).

(xi) Surface tension and viscosity ________ temperature dependent functions. (are not/are)

(xii) Liquids having regularly shaped molecules have ________ viscosity than those of irregularly shaped ones. (more/less)

(xiii) Polymorphism is for ________ but allotropy is for ________. (elements/compounds)

(xiv) Viscosity, surface tension and vapour pressure are measured by ______, ______ and ______ respectively. (manometer /stalagomometer /viscometer)

(xv) Cu, NaCl, and diamond give ________, ________ and ____________ crystals respectively. (covalent/ metallic / molecular/ionic)

(xvi) Heat is ________ when gaseous ions are allowed to form a crystal. (evolved/absorbed)

(xvii) Crystal lattice is a ________ arrangement of particles. (one dimensional /three dimensional)

(xviii) Evaporation causes ________. (cooling/heating)

(xix) Vacuum distillation is the process in which boiling point of a liquid is ________. (increased/decreased)

(xx) Transition temperature only exists for ________. (compounds/elements/both elements & compounds)

(xxi) Ionic crystals are ________ conductors of electricity in solid state but are ________ conductors in molten state. (good/bad)

(xxii) Lattice energy is also called ________ energy. (Ionization/crystal)

(26) Explain the following giving reasons:

(a) Cleavage is an anisotropic behaviour.

(b) Isomorphous substances have almost same ratio of atoms.

(c) Transition temperature is exhibited by both elements and compounds.

(d) Unit cell dimensions give us crystal system.

(e) Metallic crystals are good conductors of electricity but ionic crystals are not.

(f) Covalent crystals are very hard but molecular crystals are very soft.

4

STRUCTURE OF ATOM

subatomic particles and consequently, the development of our knowledge about the structure of atom is a result of several experimental observations. Following are some of the experiments which convince us about the divisibility of atom.

(i) Study of electric discharge through gases at low pressure.

(ii) Radioactivity.

(iii) X-rays.

(iv) Spectroscopic studies.

4.2 Nature of Charged Particles

Let us now consider some aspects of the nature of charged particles.

(i) An electric current is the movement of charged particles in a conductor.

(ii) Oppositely charged particles attract each other and particles having similar charges repel each other.

(iii) Charged particles moving between two metal plates or electrodes, one of which carries a positive charge and the other a negative charge, are deflected towards oppositly charged plates.

(iv) Charged particles when moving in a magnetic field, *e.g.*, between the two poles of a magnet are also deflected but at right angle to the lines joining the north and south poles.

(v) A sharp beam of charged particles can be obtained by using slits or holes to screen out all particles except those travelling in the desired direction.

(vi) As the charged particles are not visible their presence and direction of movement can be revealed by using a photographic film or a fluorescent material. A fluorescent material is a compound which emits faint visible light by absorbing radiant energy.

(vii) The force of attraction or repulsion between two charges can be determined by Coulomb's law.

4.3 Study of Electric Discharge Through Gases at low Pressure

Discovery of Electron

A gas-discharge tube is a glass tube having two electrodes sealed into it. It may contain a gas, air or vapours of a substance at very low pressure. A 'neon sign' is also a discharge tube which contains neon gas at a pressure of about 10 torr. In an experiment, a gas-discharge tube may be connected to a vacuum pump so that the conduction of electricity through a gas may be studied at any value of low pressure. A slit is placed in the tube, if necessary, to get a sharp beam of radiations. A simple gas discharge tube is shown in Fig 4.1.

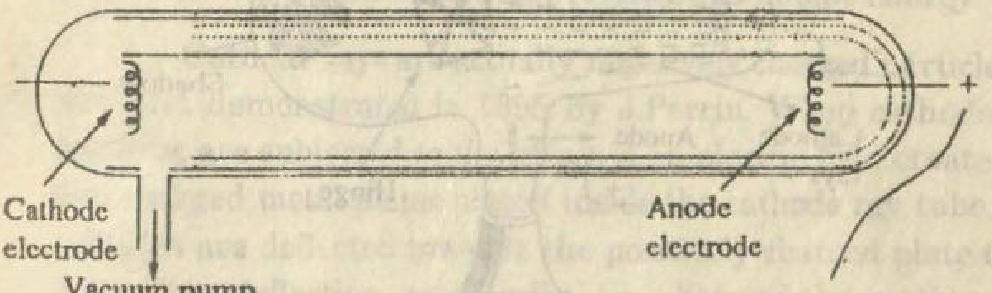


Fig. 4.1 — Schematic diagram of a gas-discharge tube (cathode ray tube).

William Crooks, a British scientist, during the late nineteenth century conducted a series of experiments using a gas-discharge tube to study the passage of electric discharge through gases. He observed that at ordinary pressure the air inside the tube did not conduct electricity even when the electrodes were connected to a source of very high potential of about 5000 volts. But when the pressure in the tube was reduced by removing most of the air with the help of a vacuum pump, an electric discharge took place through the gas producing a uniform glow inside the tube. That is, the gas in the tube begins to conduct electricity at low pressure. By reducing the pressure in the tube still further to about 0.01 torr the

original glow disappears. At this point, cathode rays are produced which produce fluorescence on striking glass opposite to the cathode. When various gases and vapours were used in discharge tube with various metals used as electrodes, the rays produced are the same. These rays are called cathode rays.

4.3.1 Cathode Rays

The first important discovery about the nature of cathode rays was made by Hittorf in 1869. He observed that objects placed in the path of these rays inside the tube cast shadow. This can easily be demonstrated by a specially designed tube as shown in Fig. 4.2.

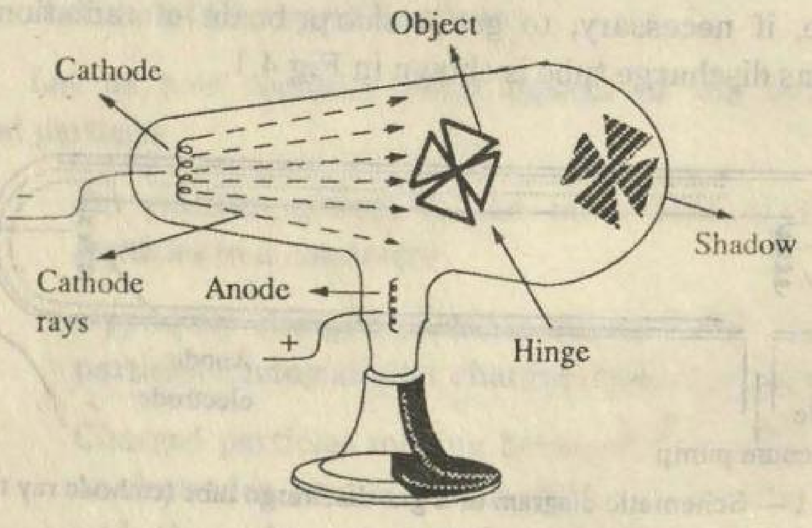


Fig. 4.2 — Crooks discharge tube for demonstrating that cathode rays cast a sharp shadow on a fluorescent screen and therefore cathode rays travel in straight lines.

Crooks in 1870 demonstrated that the cathode rays are actually streams of particles which possess kinetic energy and momentum.

Fig. 4.3. shows a cathode ray tube which has a light pin wheel inside the tube. The cathode rays exert a force on the paddles of the wheels and roll it along a double track towards the anode. When the anode is changed into cathode by reversing the direction of current the wheel begins to roll in the reverse

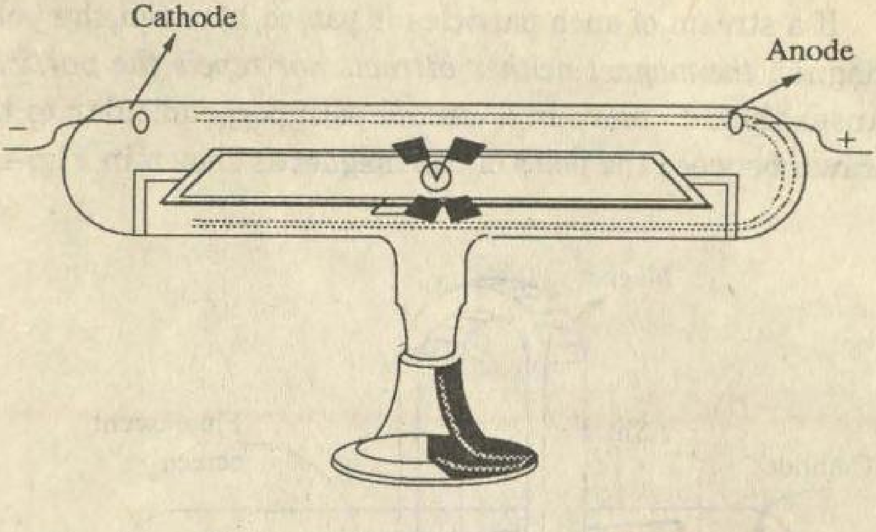


Fig. 4.3 — Discharge tube to demonstrate that cathode rays can turn a light pinwheel. Cathode rays must therefore be particles which possess mass.

direction. From this experiment Crooks concluded that the cathode rays consist of beams of particles which possess momentum and therefore mass, velocity and kinetic energy.

Cathode rays are actually negatively charged particles. It was first demonstrated in 1895 by J.Perrin. When cathode ray particles are subjected to the effect of an electric field created by two charged metal plates placed inside the cathode ray tube, the particles are deflected towards the positively charged plate (Fig. 4.4). The deflection can easily be observed by noting the movement of a bright spot formed where cathode rays strike the tube.

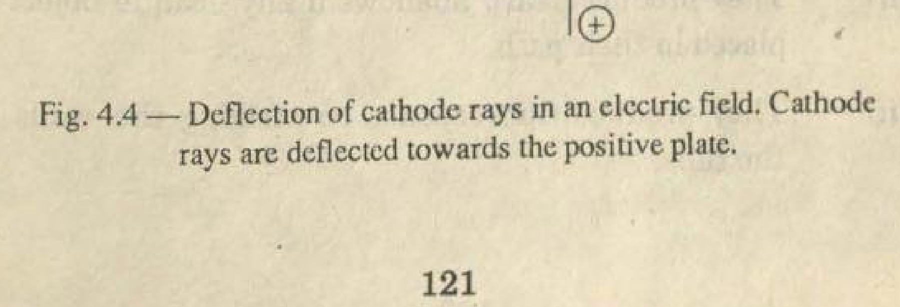


Fig. 4.4 — Deflection of cathode rays in an electric field. Cathode rays are deflected towards the positive plate.

If a stream of such particles is passed between the poles of a magnet, *the magnet neither attracts nor repels the particles* but causes them to move in a curved path perpendicular to the line drawn between the poles of the magnet as shown in Fig. 4.5

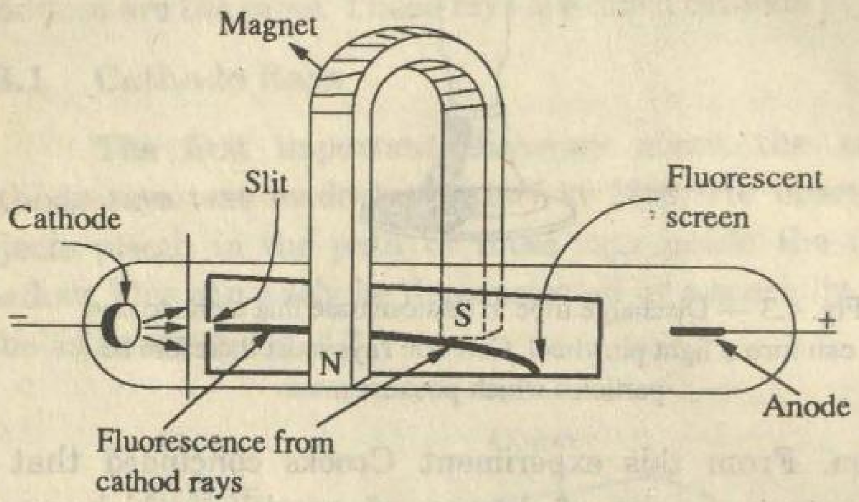


Fig. 4.5 — Deflection of cathode rays in a magnetic field.

Cathode rays also heat up a thin metal foil to incandescence when placed in their path. The cathode rays thus behave like a stream of negatively charged particles. These negatively charged particles were called electrons by G.J. Stoney (1891).

Characteristics of Cathode Rays

The above mentioned experiments indicate that the cathode rays possess the following characteristics:

(i) These rays travel in a straight line perpendicular to the cathode surface, unless acted upon by an outside force.

(ii) They produce sharp shadows if any opaque object is placed in their path.

(iii) They produce fluorescence on striking the walls of the tube.

(iv) These rays heat the object on which they fall.

(v) They can move a small light pin wheel placed inside the cathode ray tube indicating that they consist of beams of particles.

(vi) Their straight path is changed by the application of electric and magnetic fields and this behaviour indicates that they are negatively charged particles.

(vii) The nature of the cathode rays is the same irrespective of the gas used in the tube.

4.3.2 Charge to Mass Ratio of Cathode Rays

The mass (m) and charge (e) of the cathode ray particles (electrons) were determined by two famous experiments conducted by J.J. Thomson in 1897 and R.A. Millikan in 1909. J.J. Thomson could not determine the charge or mass of the electron separately. He could however, determine the charge to mass ratio e/m by subjecting and balancing a beam of cathode rays to the simultaneous effects of electric and magnetic fields (Fig. 4.6).

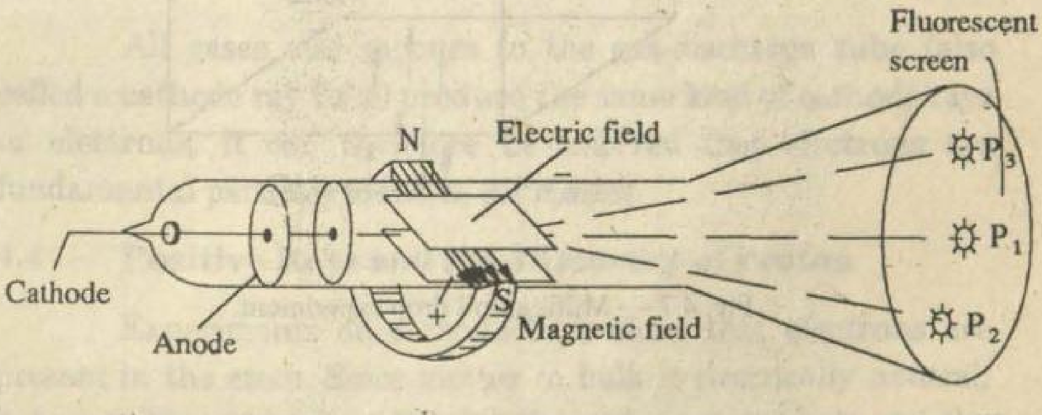


Fig. 4.6 — Schematic diagram of the apparatus used by J.J. Thomson to measure e/m of an electron.

In the absence of any electric and magnetic field, the electrons strike at P_1 on the fluorescent screen. Under the effect of electric field, they strike at P_2. Under the effect of magnetic

field alone, they strike at P_3. Electric and magnetic fields are adjusted such that electrons again strike at P_1. From the balancing of forces e/m is evaluated. The value of e/m is 1.75 x 10^{11} Coulomb/Kg.

4.3.3 Charge of Electrons

R.A. Millikan determined the charge, e, on the electron by introducing tiny droplets of an oil between two positively and negatively charged plates kept in a small chamber (Fig. 4.7).

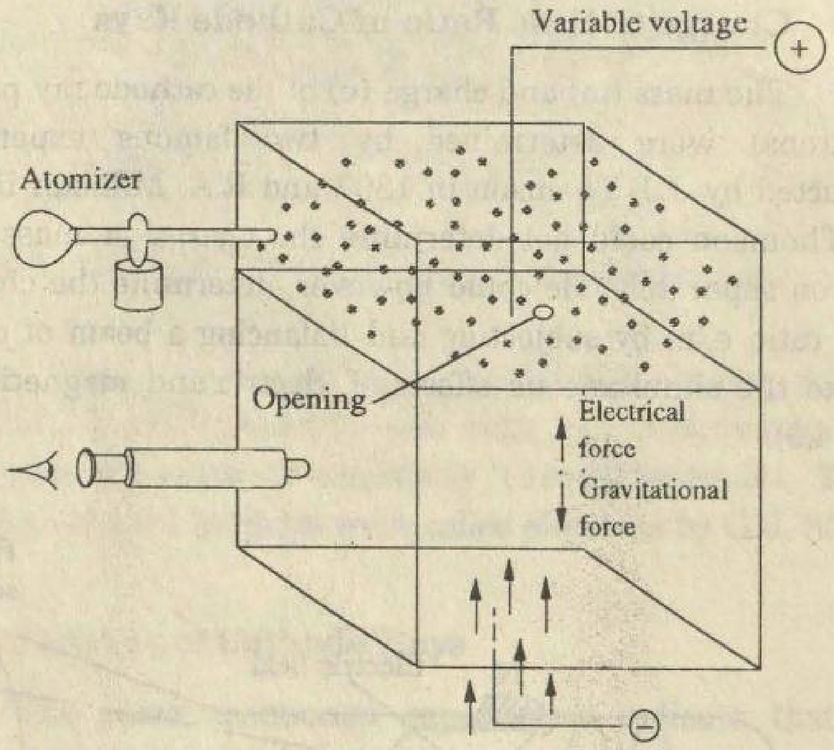


Fig. 4.7 — Millikan oil drop experiment.

The oil droplets are charged by friction while passing the atomizer. First the rate of fall of a droplet under the effect of gravity alone and then its rate of rise and fall under the effect of electric field between positive and negative plates are measured. From these rates as well as from the viscosity of air in the chamber, density of oil and strength of electric field the charge on the oil droplet can be calculated. Millikan and his co-workers

determined the charge on several thousand droplets. They found that the charge on the droplets was always 1.60×10^{-19} coulomb (symbolic) or some multiple of it. Thus the smallest charge present on a droplet is 1.6022×10^{-19}C. This is the charge acquired by a droplet when it picks up one electron from the air in the chamber.

From the values of e/m and e, the mass of the electron can be calculated as follows:

$$\frac{e}{m} = 1.7588 \times 10^{11} \text{ C/kg}$$

Since $\quad e = 1.6022 \times 10^{-19}$ C

$$\frac{1.6022 \times 10^{-19} \text{ C}}{m} = \frac{1.7588 \times 10^{11} \text{ C/kg}}{1}$$

$$m = \frac{1.6022 \times 10^{-19}}{1.7588 \times 10^{11}} \text{ kg}$$

$$= 9.1096 \times 10^{-31} \text{ kg}$$

All gases and vapours in the gas-discharge tube (also called a cathode ray tube) produce the same kind of cathode rays or electrons. It can therefore be inferred that electrons are fundamental particles found in *all* matter.

4.4 Positive Rays and the Discovery of Proton

Experiments on cathode rays show that electrons are present in the atom. Since matter in bulk is electrically neutral, it must have some positively charged part to balance the negative charge on the electrons in a given atom.

Earlier in 1886, Eugene Goldstein had performed a series of experiments in which he used a special discharge tube with a perforated cathode (Fig. 4.8). He had observed fluorescence at the end of the tube opposite the anode (positive electrode).

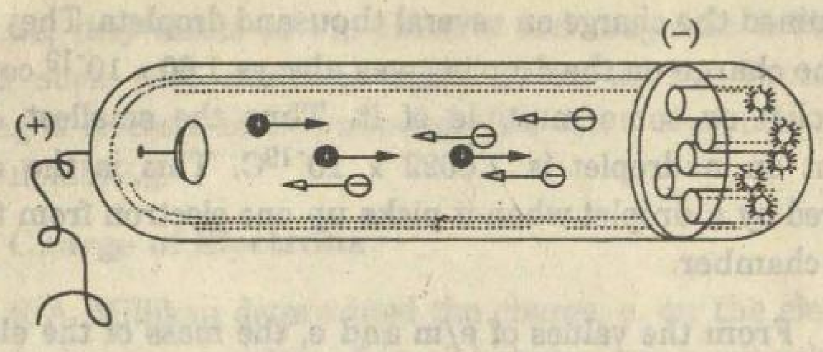


Fig. 4.8 — Canal rays. Positively charged anode rays pass through perforations in the cathode and are detected on the fluorescent screen opposite to the anode.

The fluoresence is due to rays which are flowing in the opposite direction to the cathode rays. These rays are named *canal rays,* because they pass through 'canals'-openings cut into the cathode. Because of the direction of the beam, we can conclude that it must be due to the presence of positively charged particles. The canal rays or positive rays are in fact positive ions produced by collision of cathode rays with residual gas atoms in the tube These ions are attracted to the cathode but some of the ions pass through the holes in the cathode and appear as a stream of particles on the other side.

Some of the characteristic properties of positive rays are:

(i) These rays travel in a straight line and are deflected by electric and magnetic fields in a way that reveals their positive charge.

(ii) The ratio of charge to mass, (e/m) for these positively charged rays is considerably smaller than for electrons.

(iii) The e/m ratio of the positive rays depends upon the nature of the gas in the tube. The highest e/m ratio is obtained if hydrogen gas is present.

(iv) The mass of the positive particle is never less than that of a proton.

The lightest and simplest canal ray particles are formed when a gas-discharge tube contains hydrogen. The positive

charge of this hydrogen ion was found to be 1.6022×10^{-19} coulomb which is just equal to the negative charge of the electron. From the e/m value of hydrogen ion the mass of hydrogen ion was calculated to be 1.6726×10^{-27} kg. This positive ray particle or hydrogen ion is now called proton. Rutherford later showed that proton is also a fundamental particle.

4.5 Radioactivity

In 1895, Henri Becquerel discovered that certain elements such as radium, uranium, thorium etc. emit radiations which cause fogging of photographic plates. The phenomenon of

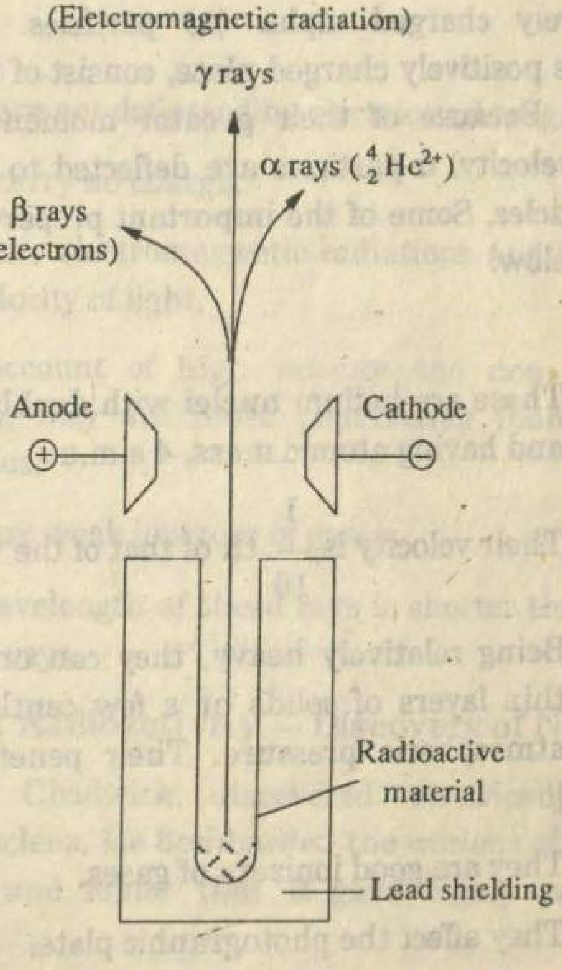


Fig 4.9 — Radiations from a radioactive material in an electric field. Heavier positively charged α-rays show less deflection, lighter negatively charged β-rays show greater deflection. γ-rays are neutral and are unaffected by the field.

spontaneous emission of nuclear radiations from a radioactive substance is called radioactivity. Elements which emit such radiations are called *radioactive elements.* The nature of radiations emitted by radioactive elements can be studied as described below.

The radioactive material is enclosed in a lead block which absorbs all the radiations except those passing through the hole. When a beam of these radiations is passed through an electric field it splits into three beams (Fig. 4.9). The undeflected rays are called gamma (γ) rays.

The beam attracted towards the negatively charged plate are positively charged alpha (α) particles. Those deflected towards the positively charged plate, consist of beta (β) particles (electrons). Because of their greater momentum (product of mass and velocity) α-particles are deflected to a smaller extent than β-particles. Some of the important properties of these rays are given below:

α - Rays

(i) These are helium nuclei with doubly positive charge and having atomic mass, 4 a.m.u.

(ii) Their velocity is $\frac{1}{10}$ th of that of the velocity of light.

(iii) Being relatively heavy, they can only pass through thin layers of solids or a few centimetres of gas at atmospheric pressure. Their penetrating power is low.

(iv) They are good ionizers of gases.

(v) They affect the photographic plate.

(vi) They are deflected by electric and magnetic field.

β - Rays

(i) They are fast moving electrons like the cathode rays.

(ii) They have a velocity about ten times greater than that of α - rays

(iii) Due to smaller size they can penetrate a few mm into metals. Their penetrating power is 100 times that of α - particles.

(iv) Their e/m ratio resembles that of electrons.

(v) Their power of ionizing the gaseous molecules is much less than that of α - particles.

(vi) They are deflected by electric and magnetic field.

γ - Rays

(i) They are not deflected by electric and magnetic fields.

(ii) They carry no charge.

(iii) They are electromagnetic radiations and travel with the velocity of light.

(iv) One account of high velocity and non - material nature, they are more penetrating than α and β particles.

(v) They are weak ionizers of gases.

(vi) The wavelength of these rays is shorter than most of the x - rays.

4.6 Artificial Radioactivity — Discovery of Neutron

In 1932 Chadwick discovered electrically neutral particles in the nucleus. He bombarded the nucleus of beryllium with α particles and found that it gave highly penetrating radiation.

This radiation knocked protons out of paraffin with great force (Fig. 4.10)

Chadwick recognized that only a neutral particle with mass close to that of a proton could knock proton out of paraffin. These particles are now called neutrons, Fig.4.10. Neutrons have

also been accepted now as fundamental particles of an atom in addition to protons and electrons.

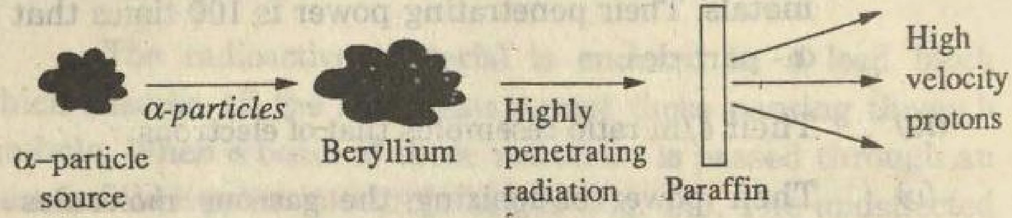


Fig. 4.10

This phenomenon of the emission of radiations from nuclei of lighter atoms due to bombardment of moving particles is known as artificial radioactivity. Examples of nuclear reactions taking place by α - particle bombardment are:

$$Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1 + Q \quad ...... (i)$$

$$_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1 \quad ... (ii)$$

$$_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{15}P^{30} + {}_0n^1$$

$$_{15}P^{30} \longrightarrow {}_{14}Si^{30} + {}_1e^0 \quad ... (iii)$$

In *(i)* a neutron and in *(ii)* a proton is ejected whereas in *(iii)* a neutron and a positron is emitted.

In all these nuclear reactions, we have bombarded stable isotopes of $_4Be^9$, $_7N^{14}$, $_{13}Al^{27}$ with helium nuclei or α (particles). As a result of this bombordment the nuclei of these atoms are broken, new atoms are produced and some radiation is emitted. This is artificial disintegration and it clearly shows that atom is divisible.

4.7 Properties of Sub - atomic Particles

The three kinds of sub-atomic particles of the atoms are:

Electron

(*i*) It has a mass 1/1836 times that of hydrogen atom and a negative charge of 1 unit.

Proton

(*ii*) It has a mass equal to that of a hydrogen atom and a positive charge of 1 unit.

Neutron

(*iii*) It has a mass almost equal to that of a hydrogen atom but no electric charge.

Some of the properties of these fundamental particles are given in Table 4.1.

Table 4.1

Properties of the Electron, Proton, and Neutron

Particle	Mass(kg)	Charge(C)	Mass(amu)	Chg(e)
Electron	9.1094×10^{-31}	-1.60218×10^{-19}	0.00055	-1
Proton	1.6726×10^{-27}	$+1.60219 \times 10^{-19}$	1.0073	+1
Neutron	1.67493×10^{-27}	0	1.0087	0

Our present information indicates that the diameter of an atom is somewhat greater than 10^{-10} m and an atom contains a very tiny nucleus with a diameter less than 10^{-14}m or about $^{1}/_{1000}$ that of an atoms as a whole. The atom is made up of protons, electrons and neutrons. Protons and neutrons are present in the nucleus but electrons reside around the nucleus. Number of protons is equal to number of electrons in the atom.

Uptil now more than 100 elementary particles have been discovered. However for most purposes, a chemist is usually interested in only three fundamental particles, the electron, proton and neutron.

4.8 X - Rays and Atomic Number

In 1895, W.C. Roentgen discovered that when high energy electrons (cathode rays) collide with the anode, a very penetrating kind of radiation is produced. Roentgen called them x-rays (Fig 4.11)

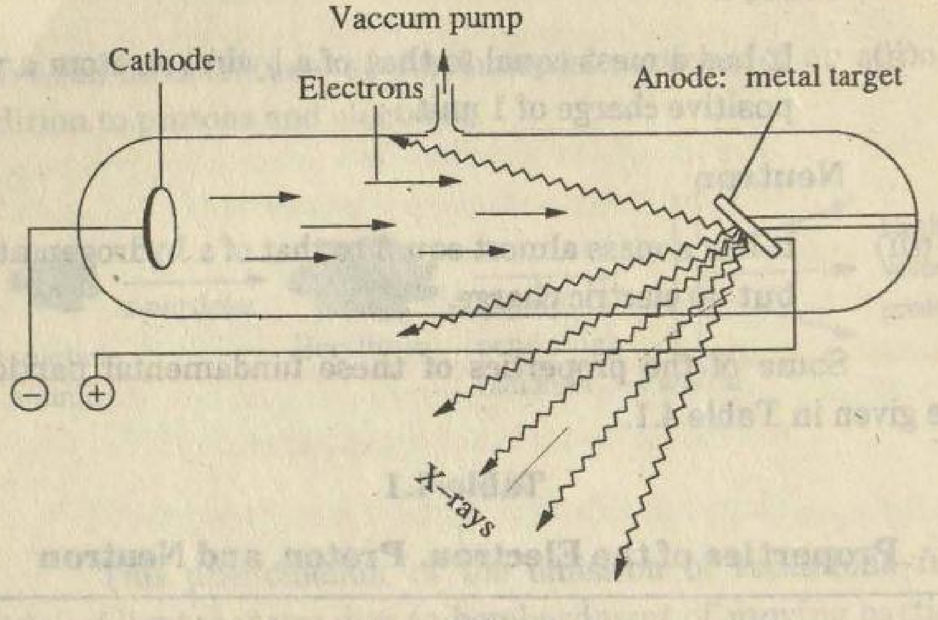


Fig. 4.11 — An x-ray tube

X-rays are electromagnetic radiations of very high frequency. The frequency of the x-rays depends on the material used as the anode. In 1913 Mosley was able to show that the frequencies of emitted rays increase with the number of positive charges on the nuclei of target element and that they increase from element to element by a single electron unit. This number of positive charge on the nucleus of an atom of an element is now called the *atomic number* denoted by Z. As each proton has a unit positive charge, the atomic number Z of an element is number of protons contained in the atom.

4.9 Scattering of α-Particles and Discovery of Nucleus

Rutherford bombarded thin gold foil with α–particles, from a radioactive material as shown in Fig. 4.12a. The α-particles emerge from source at the left and strike a thin metal foil. Most of the particles go straight through the foil. A few are deflected through various angles and some are even deflected backward. According to Rutherford, the regions which deflect the positive α - particles must bear a heavy positive charge present in an atom. This part of the atom is called nucleus. Only a small volume of the atom is occupied by the nucleus but, most of the volume of the atom is occupied by the extra nuclear

electrons. Rutherford's experiment indicates that the positive charge of atom is concentrated at its centre called nucleus. (Fig. 4.12b).

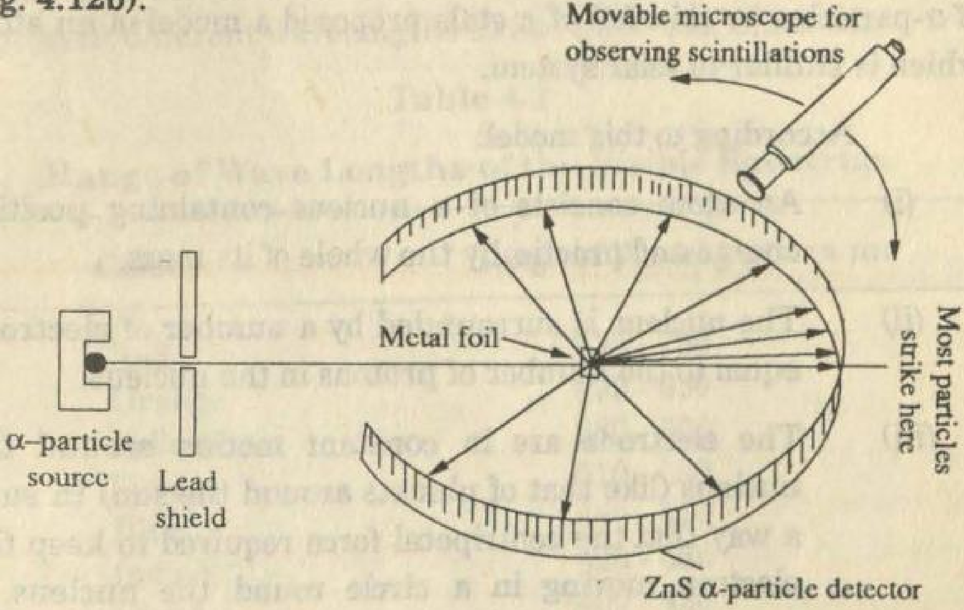


Fig. 4.12 (a) — Rutherford's experiment. Positively charged α-particles from a radioactive source are scattered by a thin metal foil. Scattering occurs in all directions as detected by fluorescence on ZnS detector

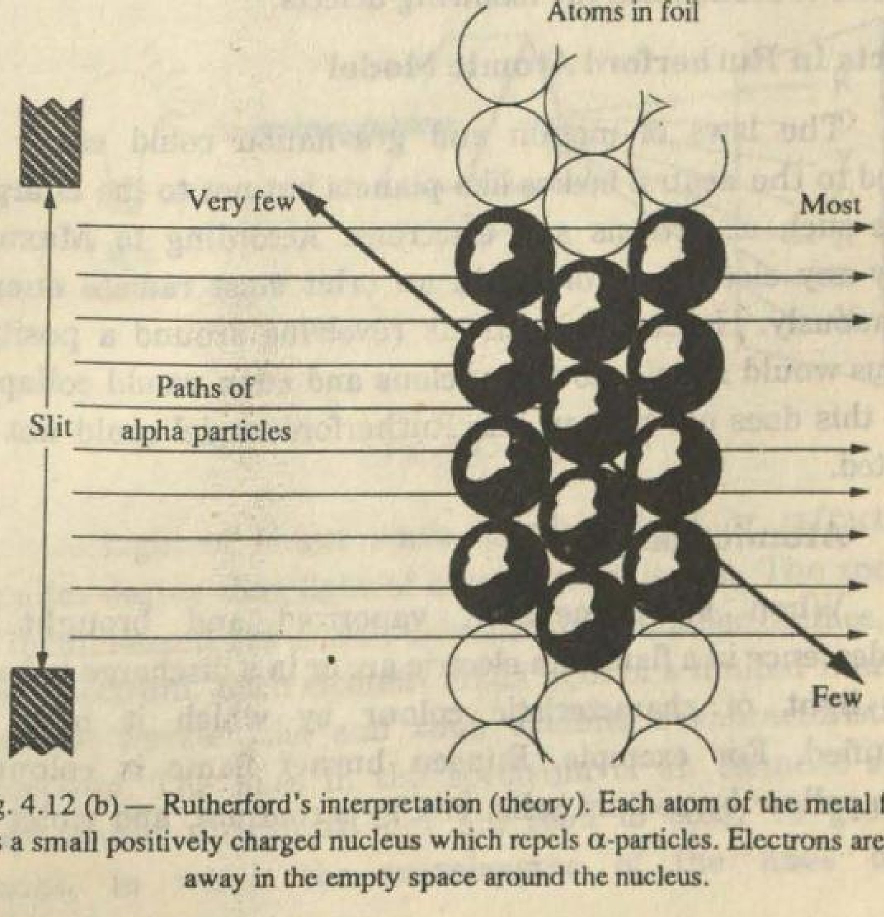


Fig. 4.12 (b) — Rutherford's interpretation (theory). Each atom of the metal foil has a small positively charged nucleus which repels α-particles. Electrons are far away in the empty space around the nucleus.

4.10 Rutherford's Model of An Atom

Rutherford on the basis of his experiments on scattering of α-particles by thin foil of metals proposed a model of an atom which is similar to solar system.

According to this model:

(i) An atom consists of a nucleus containing positive charge and practically the whole of its mass.

(ii) The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.

(iii) The electrons are in constant motion around the nucleus (like that of planets around the sun) in such a way that the centripetal force required to keep the electron moving in a circle round the nucleus is provided by the electrostatic force of attraction between the electrons and nucleus.

This model of atom which was based on the gravitation and laws of motion had the following defects.

Defects in Rutherford Atomic Model

The laws of motion and gravitation could easily be applied to the neutral bodies like planets but not to the charged bodies such as protons and electrons. According to Maxwell theory any electron revolving in an orbit must radiate energy continuously. Hence the electrons revolving around a positive nucleus would spiral into the nucleus and atom would collapse. Since this does not happen, the Rutherford model could not be accepted.

4.11 Atomic Spectra

When an element is vaporized and brought to incandescence in a flame, an electric arc or in a discharge tube, it emits light of characteristic colour by which it may be indentified. For example, Bunsen burner flame is coloured golden yellow by sodium salts, red by strontium, and violet by

potassium. In a discharge tube neon glows with an orange red colour and helium with pink colour. Light of different colours represent different wavelengths as shown in the Table 4.2.

Table 4.2

Range of Wave Lengths of the Visible Spectrum

Colour	Range of Wavelength in nm
Red	630 - 750
Orange	600 - 630
Yellow	580 - 600
Green	510 - 580
Blue	460 - 510
Indigo	420 - 460
Violet	400 - 420

When white light is passed through a prism it spreads out into a spectrum as shown in Fig 4.13.

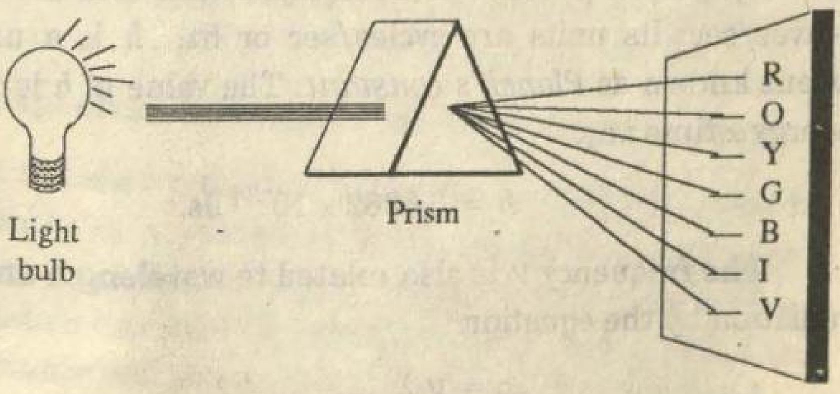


Fig. 4.13

Light of longer wave length is bent or refracted, to smaller degree than light of shorter wave length. The spectrum of incandescent gas is seen to consist of a number of lines, called line spectrum. Each element emits light of a limited number of definite wavelengths and thus exhibits a characteristic line spectrum. The lines in the spectrum of an element are not haphazardly distributed but are seen to occur in groups or series, in which the wavelengths of the lines bear a

mathematical relationship to one another. In each series the lines converge *i.e.*, the separation between them decreases regularly as their wavelengths decrease reaching a limiting value beyond which the spectrum becomes continuous.

The spectrum of the sun or of incandescent solids *e.g.*, electric light etc. is continuous. In such a spectrum the boundary lines between the colours cannot be marked, because the colours diffuse into each other.

4.11.1 Planck's Quantum Theory of Radiation

Max Planck in 1900 explained the emission of light energy by proposing that light was produced by vibrating groups of atoms, and that light energy (or all sorts of radiations) could only be absorbed or given out by vibrating atoms, according to the equation.

$$E = h\bar{\nu} \quad .... 4.1$$

Where E is the energy given out or absorbed by atoms, ν is the frequency of photon absorbed or emitted. It is the number of waves/sec. Its units are cycles/sec or hz. h is a universal constant known as *Planck's constant*. The value of h is in units of energy x time *i.e.*,.

$$h = 6.6262 \times 10^{-34} \text{ Js.}$$

The frequency ν is also related to wavelength and speed of radiation by the equation

$$c = \nu\lambda \quad .... 4.2$$

$$= 3.00 \times 10^{8} \text{ms}^{-1}$$

Where c is the speed of light and λ is the wavelength of any light radiation. Wavelength is the distance between two successive crests or troughs. Its units are m (or cm).

Another term wave number $\bar{\nu}$ of the photon of radiation is the number of waves/unit distance. It is inverse of wave length $(\lambda)^{-1}$. Its units are

$$\bar{\nu} \propto \frac{1}{\lambda}$$

or

$$\lambda = \frac{1}{\bar{\nu}}$$

or

$$\lambda = \frac{c}{\bar{\nu}}$$

or

$$\bar{\nu} = \frac{c}{\lambda}$$

or

$$E = \frac{hc}{\lambda} \quad \text{..............................} \quad 4.3$$

These relationships give the information about the dependence of energy of photon of light on frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$).

An instrument that measures the intensity and frequency of emitted or absorbed radiation is called a spectrometer.

4.11.2 Line Spectra - Emission and Absorption Spectra

When radiation consisting of all wave lengths are passed through a sample of a substance it may absorb a particular radiation. The spectrum of such radiations from which a particular radiation has been absorbed after passing through the absorbing substance will show a dark line in a continuous band.

When a substance that has absorbed energy emits it in the form of radiation, the spectrum is an emission spectrum.

Continuous emission spectrum from a source of white light, line emission spectrum from hydrogen gas-discharge tube and absorption line spectrum of hydrogen are shown in Fig. 4.14.

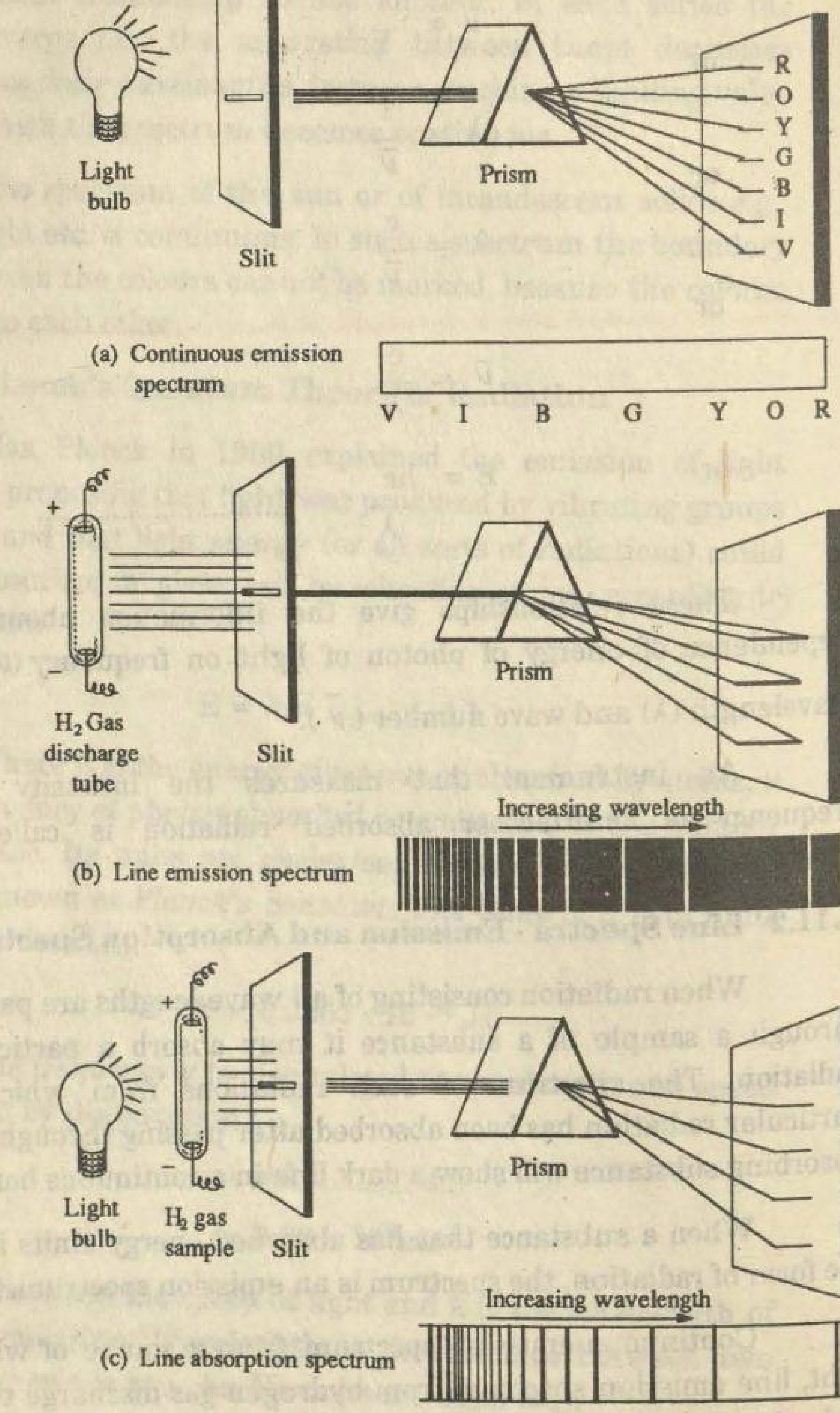


Fig. 4.14 (a) — Continuous emission spectrum. Light consisting of all wavelengths when passed through a prism is separated into various colour bands.

(b) — Atomic emission spectrum. Light emitted by a sample of excited hydrogen atoms when passed through a prism is separated into discrete wavelengths.

(c) — Atomic absorption spectrum. White light when passed through unexcited hydrogen and then through a prism lacks in intensity at the same wavelengths as are emitted in (a).

In the Fig. 4.14, you have noticed that hydrogen which is the simplest of all atoms produces discrete line spectra. The frequency, wavelength and energy of these lines can be determined with the help of a spectrometer. Notice that the emission lines and absorption lines are exactly at the same place, i.e., the energies of radiations emitted by excited hydrogen are exactly the same as the energies of radiations absorbed by cold hydrogen.

4.12 Bohr Model of Hydrogen Atom

How can we explain the line spectrum of hydrogen? If the electron of hydrogen atom is moving around the nucleus, it must follow a curved path and as discussed in section 4.10 must lose energy by emitting continuous band of radiations and consequently spiral into the nucleus. Bohr in 1913 developed a model of hydrogen atom to overcome these difficulties by making the following four assumptions.

(i) The electron in the hydrogen atom can only move around the nucleus in a circular way.

(ii) Electron does not radiate energy as long as it remains in one of the orbits.

(iii) The electron loses the energy, when it jumps from higher to lower orbit and absorbs when it jumps from lower to higher one. The energy difference between any two levels is:

$$\Delta E = h\nu$$

(iv) The angular momentum of electron of a hydrogen atom can only be a whole number multiple of $h/2\pi$, that is angular momentum is quantized.

$$\text{angular momentum } mvr = \frac{nh}{2\pi} \quad \ldots\ldots\ldots\ldots \quad 4.4$$

Where n is any whole number 1,2,3,4 .... etc, and; m is the mass of electron, v its velocity, r the radius of the electronic orbit and h is the Planck's Constant.

Based on these assumptions Bohr not only presented a model of hydrogen atom that explained the spectrum of hydrogen but also a model for all other atoms as well.

Bohr assumes that nucleus of hydrogen atom (proton) being 1836 times heavier than electron can be considered at rest relative to the electron. The electron moves in an orbit at a distance r from the nucleus as shown in Fig. 4.15.

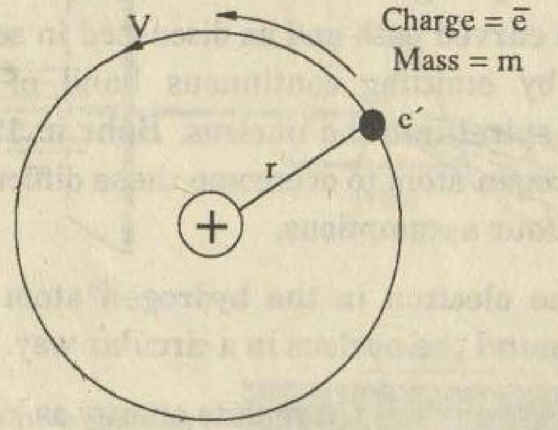


Fig. 4.15 — A hydrogen atom.

For uniform circular motion, the electron must be acted upon by a centripetal force directed toward the centre (nucleus) of the orbit. This centripetal force is given by the expression:

$$F = \frac{mv^2}{r} \quad \text{.............................} \quad 4.5$$

Where v is the velocity of the electron. The centripetal force is being provided by the coulombic force of attraction between the nucleus and the electron.

According to Coulomb's law the force between two charges Q_1 and Q_2 separated by a distance r is

$$F_{coul} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2} \quad \text{.................} \quad 4.6$$

Where ϵ_0, (Greek letter ϵ called epsilon) the *permitivity of the vacuum* is proportionality constant with numerical value $8.854 \times 10^{-12}\ C^2J^{-1}m^{-1}$.

In case of electron the coulombic force is given by:

$$F_{coul} = \frac{Ze \times e}{4\pi\epsilon_0 r^2} \quad \text{.................} \quad 4.7$$

Where Ze is the charge on the nucleus, (The value of Z, the atomic number for hydrogen is 1 and e is the charge on electron).

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 r^2} \times \frac{r}{m}$$

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 rm} \quad \text{....................} \quad 4.8$$

Applying Bohr assumption $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2h^2}{4\pi^2r^2m^2} \quad \text{....................} \quad 4.9$$

Equating 4.8 and 4.9

$$\text{or} \quad \frac{Ze^2}{4\pi\epsilon_0 rm} = \frac{n^2h^2}{4\pi^2r^2m^2}$$

Solving for r gives

$$r = \frac{\epsilon_0 n^2 h^2}{\pi Z e^2 m} \quad \text{.................} \quad 4.10$$

$$r = \frac{n2}{Z} \times \frac{\epsilon_0 h^2}{\pi e^2 m}$$

$$r = \frac{n^2}{Z} \times a_0 \quad \text{.............} \quad 4.11$$

where, $$a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m} \quad \text{...................} \quad 4.12$$

Where a_0 is called Bohr radius and has a numerical value 5.29×10^{-11}m = 0.529 A°. A° is a unit of length called Angstrom unit. (1A° = 10^{-10}m = 10*nm*).

The radius of first Bohr's orbit for hydrogen for which the value of n = 1 and Z = 1, from 4.1

$r = a_0$

Example 1

Calculate the radius of electron orbit of a hydrogen atom for which the value of n = 2

Solution

$$r_n = \frac{n^2}{Z} \times a_0$$

$$= \frac{2^2}{1} (0.529A^o)$$

$$= 4\ (0.529A^o)$$

$$= 2.12\ A^o$$

4.12.1 Energy of Electron

The energy of the electron moving in an orbit around the nucleus is the sum of its kinetic energy due to motion and potential energy due to its interaction with the nucleus.

Thus $E = KE + PE$

$$KE = \frac{1}{2}mv^2 \quad \text{..................} \quad 4.13$$

According to Coulomb's law the potential energy of interaction of two charges Q_1 and Q_2 separated by a distance r.

$$PE = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$$

For a nucleus of charge + Ze and an electron of charge-e this potential energy takes the form

$$PE = -\frac{Ze \times e}{4\pi\epsilon_0 r} \quad \text{.....................} \quad 4.14$$

Where minus sign indicates a net attractive interaction, giving an algebraically lower energy at shorter distance.

The total energy is given by expression:

$$E = \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r}\right) \quad \text{......} \quad 4.15$$

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Inserting the value of v^2 from 4.8.

$$E = \frac{1}{2} m \times \frac{Ze^2}{4\pi\epsilon_0 rm} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{....} \quad 4.16$$

$$E = -\frac{Ze^2}{8\pi\epsilon_0 r}$$

Substituting the value of r from 4.10

$$E_n = -\frac{Z^2 e^4 m}{8\epsilon_0{}^2 n^2 h^2} \quad \text{..................} \quad 4.17$$

$$E_n = -\frac{e^4 m Z^2}{8\epsilon_0^2 h^2 n^2} \quad \text{..............} \quad 4.18$$

or by inserting the values of e, m, ϵ_0, h etc. 4.18 becomes.

$$E_n = -2.18 \times 10^{-18} J \frac{Z^2}{n^2} \quad \text{..............} \quad 4.19$$

The energy state charaterized by n = 1 is called the ground energy state and represents the lowest energy of the system. All energy states with values of n higher than 1 are termed as excited states, for hydrogen atom.

Also note that all quantities on right hand side in 4.17 are constant except *n* which can have any integral value 1, 2, 3, 4, ------ etc. Thus the energy of an electron depends on its value of *n* and is called the *principal quantum number* .

Example 2

Calculate the energy of electron of a hydrogen atom in the orbit for which the value of *n* = 3

Solution

$$z = 1, n = 3$$

From 4.19.

$$E_3 = -(2.18 \times 10^{-18} J) \times \frac{1^2}{3^2}$$

$$E_3 = -(2.18 \times 10^{-18} J) \times \frac{1}{9}$$

$$E_3 = -2.42 \times 10^{-19} J$$

Equation 4.18. gives the energy of electron for a particular energy state or orbit for which the value of n is known. When an electron drops from a higher energy state E_2 to

a lower energy state E_1, a definite quantity of energy is *emitted* as one photon of radiation. The energy change and the frequency of this radiation are proportional to each other according to Planck's relationship.

$$\Delta E = E_2 - E_1 = h\nu \quad \text{............} \quad 4.20$$

If the electron is to be raised from state 1 to state 2, the same quantity of energy as one photon of radiation must be *absorbed*.

Now let us calculate ΔE, the energy emitted by hydrogen atom in the form of a photon when an electron from a higher energy state n_2 (higher value of n) drops to a lower energy state n_1 (lower value of n).

$$\Delta E = E_2 - E_1 = \left(-\frac{Z^2e^4m}{8\epsilon_o^2 n_2^2 h^2}\right) - \left(\frac{-Z^2e^4m}{8\epsilon_o^2 n_1^2 h^2}\right)$$

After simplifying:

$$\Delta E = \frac{Z^2e^4m}{8\epsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{......} \quad 4.21$$

As value of Z for hydrogen atom is 1, therefore,

$$\Delta E = \frac{e^4m}{8\epsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{......} \quad 4.22$$

$$\Delta E = 2.18\times10^{-18}J\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{..} \quad 4.23$$

The frequency (ν) and wave length (λ) of the radiations emitted by hydrogen atom can also be calculated as under:

$$\Delta E = h\nu = \frac{e^4m}{8\epsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\upsilon = \frac{e^4m}{8\epsilon_o^2h^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad \ldots 4.24$$

If we want to determine the wave number $\bar{\nu}$ of the photon emitted or absorbed due to the jumping of electron between two levels n_1 and n_2, then make use of equation (4.25).

$$\nu = c\bar{\nu} \quad \ldots\ldots\ldots\ldots\ldots \quad (4.25)$$

putting (4.25) into 4.24

$$c\bar{\nu} = \frac{e^4m}{8\epsilon_o^2h^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$\bar{\nu} = \frac{e^4m}{8\epsilon_o^2h^3c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad \ldots\ldots\ldots \quad 4.26$$

$$\bar{\nu} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad \ldots\ldots\ldots \quad 4.27$$

Where R is Called Rydberg constant.

$$R = \frac{e^4m}{8\epsilon_o^2h^3c} = 1.0974 \times 10^7 m^{-1}$$

We can now test Bohr's theory by calculating the frequencies of radiations when electrons drop from higherenergy states to lower energy states and comparing these values with the experimental values obtained from the spectrum. When we do this we find that the values of the spectral lines in the visible region (Fig 4.16) correspond to the transitions from n_2 = 3, 4, 5, ... to n_1 = 2 *i.e.*, when electron jumps from third, fourth, fifth ..... orbits to the second orbit. The spectral lines indicating these transitions are known as Balmer series. Later on values of energies of other spectral lines in ultra violet region

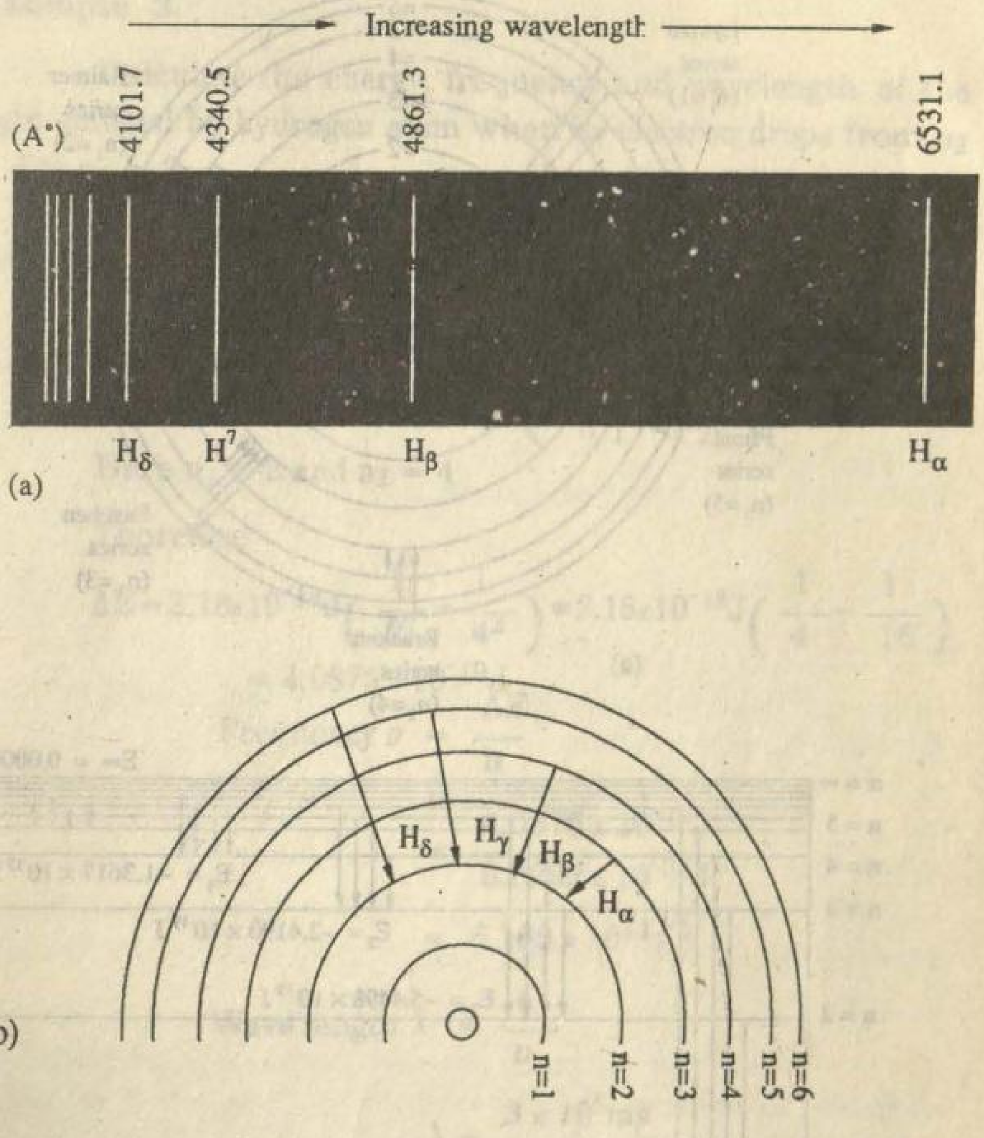
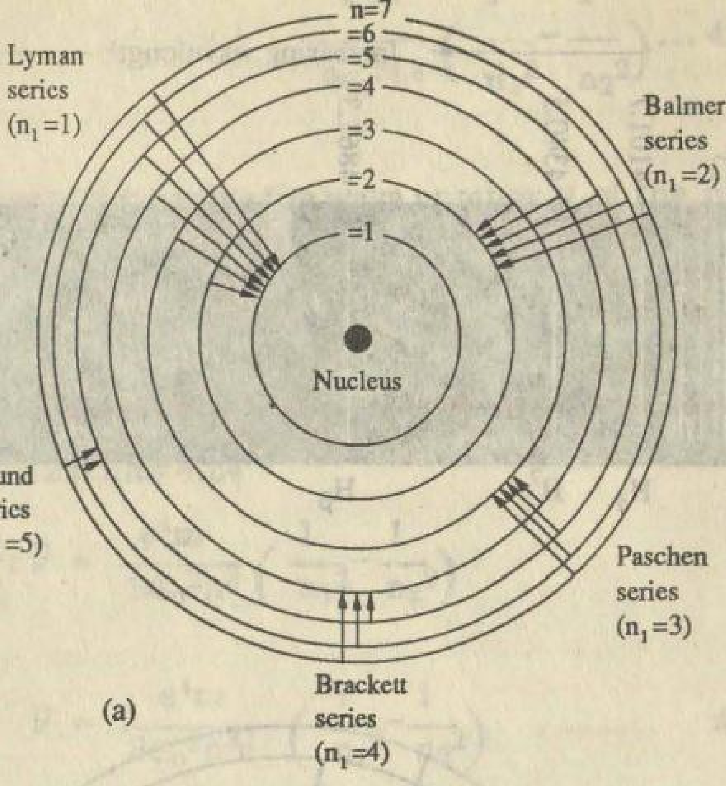
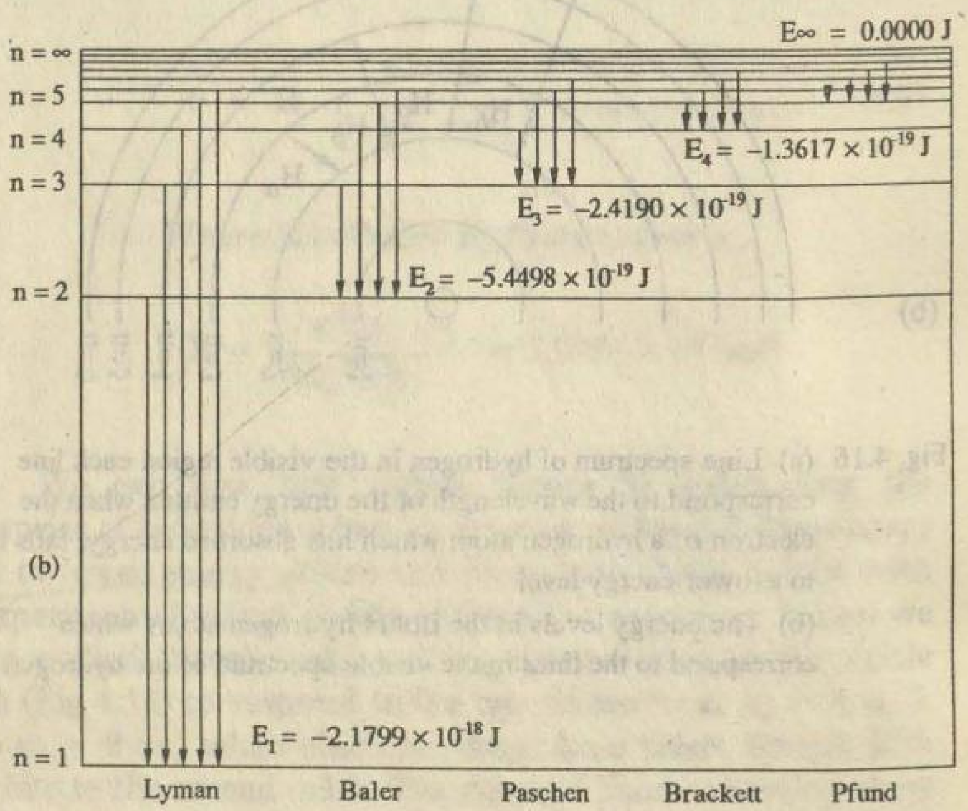


Fig. 4.16 (a) Line spectrum of hydrogen in the visible region each line correspond to the wavelength of the energy emitted when the electron of a hydrogen atom which has absorbed energy, falls back to a lower energy level.
(b) The energy levels in the Bohr's hydrogen atoms which correspond to the lines in the visible spectrum of the hydrogen atoms.

(Lyman series, Fig. 4.17) and infrared region (Paschen, Brackett and Pfund series) were also found to correlate closely with the values calculated with the help of Bohr theory (Eq. 4.21).



(a)



(b)

Fig. 4.17 (a) — The energylevels of the hydrogen atom.

(b) — The transitions seen in the emission spectrum. The separated electron and proton are arbitrarily assigned zero energy, and all other energies are more negative than that.

Example 3

Calculate the energy, frequency and wavelength of the light emitted by hydrogen atom when its electron drops from $n_2 = 4$ to $n_1 = 2$

$$h = 6.626 \times 10^{-34} JS \qquad C = 3 \times 10^{8} ms^{-1}$$

Solution

Energy of the emitted photon is given by equation 4.23

$$\Delta E = 2.18 \times 10^{-18} J \left(\frac{1}{n^2_1} - \frac{1}{n^2_2} \right)$$

Here $n_1 = 2$ and $n_2 = 4$

Therefore

$$\Delta E = 2.18 \times 10^{-18} J \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 2.18 \times 10^{-18} J \left(\frac{1}{4} - \frac{1}{16} \right)$$

$$= 4.0875 \times 10^{-19} J$$

$$\text{Frequency } \upsilon = \frac{\Delta E}{h}$$

$$= \frac{4.0875 \times 10^{-19} J}{6.6262 \times 10^{-34} J}$$

$$= 6.169 \times 10^{14} s^{-1}$$

$$\text{Wave length } \lambda = \frac{c}{\upsilon}$$

$$\lambda = \frac{3 \times 10^{8} ms^{-1}}{6.169 \times 10^{14} s^{-1}}$$

$$\lambda = 4.86 \times 10^{-7} m$$

4.12.2 Defects of Bohr Model

This theory explains satisfactorily the stability of the atoms, ionization energy and the spectra of hydrogen and hydrogen like ions (He^{+1}, Li^{+2}, Be^{+3}) yet is fails to account for the following.

(i) It cannot predict the energy states of more complicated atoms.

(ii) It cannot account for the fine structure in the line spectrum of the hydrogen like atoms.

(iii) When the spectrum of hydrogen atom is taken in the magnetic field, some new lines are created (Zeeman effect), which cannot be explained by Bohr's theory.

4.12.3 Waves and Particles

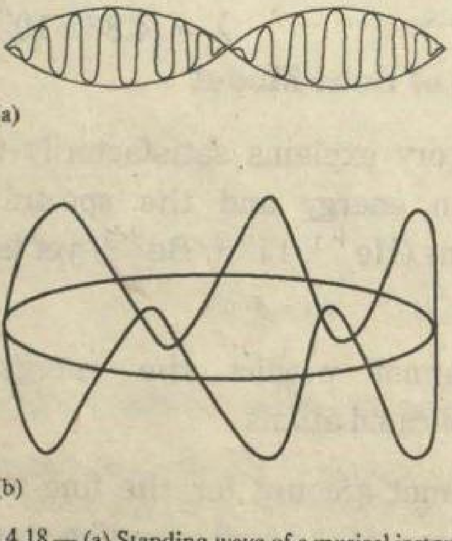
In 1905 Einstein in his theory of photoelectric effect showed that light has both wave-like and particle like properties. In 1924 a French scientist Louis de Broglie predicted that all atomic particles also have wave-like properties. The wave length of these particles, according to his predictions depends upon their mass and volecity and is given by the following equation.

$$\lambda = \frac{h}{mv} \qquad \text{.........................} \qquad (4.28)$$

Where m is the mass of the particle with a volcity v and h is the Planck's constant.

In 1927 two Amercian scientists, Davission and Germer actually showed by expriments that electrons, which had hitherto been considered as particles, were waves with very short wave length. How do electrons behave as waves in an atom?

A German physicist Erwin Schrodinger proposed that electrons in any atom may be considered as standing waves (Fig. 4.18) just like the waves produced in a string of guitar. If you



(b)

Fig 4.18 — (a) Standing wave of a musical instrument.
(b) Circular standing wave.

pluck the string, only certain discrete states of vibrations are allowed for gitar string. That is, the vibrations are "quantized". The condition on the allowed wave lengths is:

$$n = \frac{\lambda}{2} = L \quad \text{..............} \quad 4.29$$

Where n = 1, 2, 3,......., and L is the length of the string.

It is impossible to create a wave with any other value of λ if the ends of the string are fixed. The electron wave can similarly be associated with a *circular standing wave* about the nucleus of the atom. The condition on the allowed wavelengths for the *circular standing wave* is:

$$n\lambda = 2\pi r \quad \text{........................} \quad 4.30$$

Only an integral number of wave lengths must fit into the circumference of the circle $2\pi r$. Upon substituting the value of λ from equation (4.28) in (4.30).

$$n \frac{h}{mv} = 2\pi r$$

or

$$mvr = \frac{nh}{2\pi} \quad \text{........................} \quad 4.31$$

This is exactly the assumption of the Bohr's theory. Thus Bohr's assumption contains in it the concept of wave nature of electron.

4.13 Heisenberg's Principle of Uncertainity

In order to locate the *position* of an object accurately we must use light whose wave length is comparable or shorter than the size of the object. But from de Broglie's equation,

$\lambda = \frac{h}{mv}$ we find that shorter the wavelength the greater will be the momentum of the photon. We cannot make an accurate measurement of the object's momentum as it will be

knocked out from its original trajectory by the photon. Thus we cannot measure accurately both the position and momentum of an object. For a particle as small as electron, this lack of precision is critically important. An electron is so small that it is disturbed or put in unpredictable motion by an attempt to examine it. As a result of this uncertainty, the Bohr's model of atom according to which electrons travel in definite orbits and with definite momentum is not satisfactory. The best we can do is to find the *probable position* in an atom.

4.14 The Quantum Mechanical Model of Atom

In 1926 Erwin Schrodinger developed an equation in which electrons are treated as moving with wavelike motion in the three dimensional space round the nucleus, not in orbits as in Bohr's model. The schrodinger equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \text{.........} \quad 4.32$$

is a second order differential equation that describes the total energy, E, and the potential energy V of the electron in terms of its mass m with respect to its position in three dimensions x, y and z. The wave function ψ (Greek letter "psi") is such that ψ (x, y, z) is the amplitude of the wave at the point in space defined by the set of cartesion coordinates (x, y, z). The mathematics of Schrodinger equation is difficult. However approximate solutions of the Schrodinger equation for hydrogen like atoms gives much more information about atoms and molecules than the Bohr's theory. For example quantum mechanical model of atom developed on the basis of Schrodinger equation helps to calculate more accurately the energies of electrons, the bond energies, bond lengths, shapes and geometries of molecules etc.

The important consequences of the quantum mechanical description of atoms include the following:

(i) The energy of electrons in atoms is quantized.

(ii) The number of possible energy levels for atoms of different elements is a direct consequence of the wave-like properties of electrons.

(iii) The position and momentum of the electron cannot be determined simultaneously.

(iv) The region in space around the nucleus in which the electron is most probably located is what can be predicated in an atom. Electrons of different energies are likely to be found in different regions. The regions in space round the nucleus in which an electron with a specific energy is most probably located is called an *atomic orbital.*

4.15 Orbitals and Quantum Numbers

The designation of the orbital location of an electron requires four quantum numbers. Three of them arise from solutions of Schordinger equation. The fourth quantum number is due to the two ways in which an electron may be aligned in a magnetic field. These four quantum numbers which are denoted by the letters n, ℓ, m and s are called the *principal quantum number, azimuthal quantum number, magnetic quantum number* and *spin quantum number* respectively. The properties of electrons, e.g., the energy, shape of orbital, orientation in space are determined by the values of these quantum numbers.

(i) Principal Quantum Number (n)

This quantum number n may have any integral value, 1, 2, 3, 4, ...∞. The lower the value of n the lower will be the value of energy of electron while higher the value of n higher the energy.

This quantum number is same as simple integer in Bohr's equation. It appears in eq. (4.11) and (4.18). These relationships tell the distance of electron from the nucleus and its energy.

(ii) Azimuthal Quantum Number (ℓ)

This quantum number describes the shape of an orbital. It also contributes to the energy of the electron, but to a much less extent than n. It may have any value from 0, 1, 2, ... upto n—l. The value of l tells whether the orbital is spherical, a dumbell or, sausage shaped or even more complicated. If the value of l = 0 the orbital is spherical and called s orbital. If the value of l = 1, the orbital is dumbell in shape and called p orbital, when the value of l = 2, the orbital is called d orbital. If the value of l = 3, the orbital is called *f* orbital.

For example, if n = 1, l = 0, this means that the main level and sub level are one and the same, but if n = 2 then l = 0 and 1. This means that there are two sub levels of the second energy level. Similarly, if n = 3 then l = 0, 1, 2. This means that there are three sublevels of the third energy level.

(iii) The Magnetic Quantum Number (m)

This quantum number explains the magnetic properties of an electron. This also gives orientation of the orbital. The value of m varies from $-l$ to $+l$ including zero. That is:

$$m = -l \; .... \; 0 \; ..... \; +l$$

Table 4.3

Allowed Combinations of Quantum Numbers

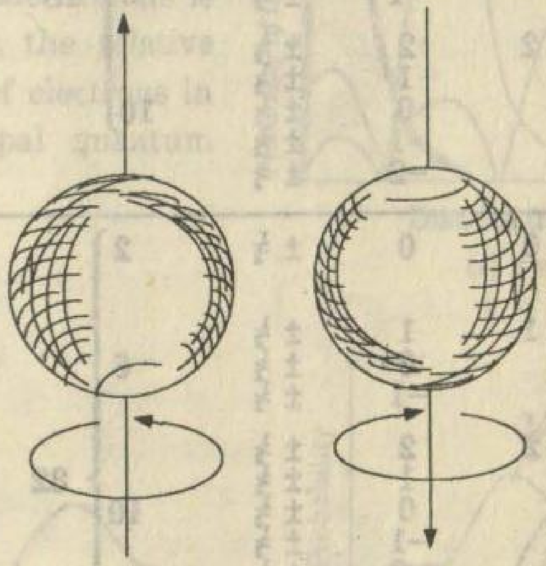
n	l	Orbital name	m
1	0	*1s*	0
2	0	*2s*	0
2	1	*2p*	-1, 0, 1
3	0	*3s*	0
3	1	*3p*	-1, 0, 1
3	2	*3d*	-2, -1, 0, 1, 2

Thus when n = 1, l = 0, m = 0, the number of orbital is one which is circular and is called s orbital. When n = 2, l = 1 and m = +1, 0, − 1 corresponding to three orbitals with their orientations parallel to three coordinate axis x, y, z and are called P_x, P_y, and P_z orbitals, respectively.

Allowed combinations of quantum numbers n, l and m are given in the Table 4.3 and possible arrangement of electrons are given in Table 4.4.

(iv) The Spin Quantum Number (m_s)

This quantum number is associated with the spin of an electron in the atom. All the electrons spin either in clockwise direction or in anticlockwise direction.



One electron has $m_s = {}^1/_2$ the other has $m_s = {}^{-1}/_2$

Fig. 4.19 — Two possible orientations of the spin of an electron about its own axis.

The direction of motion can be found out by the application of an external field since the probability of motion in each case is 50% clockwise and 50% anti-clockwise. The spin quantum number, denoted by symbol m_s has value of

$$+\frac{1}{2} \text{ or } -\frac{1}{2}$$

Table 4.4

Possible Arrangements of the Electrons

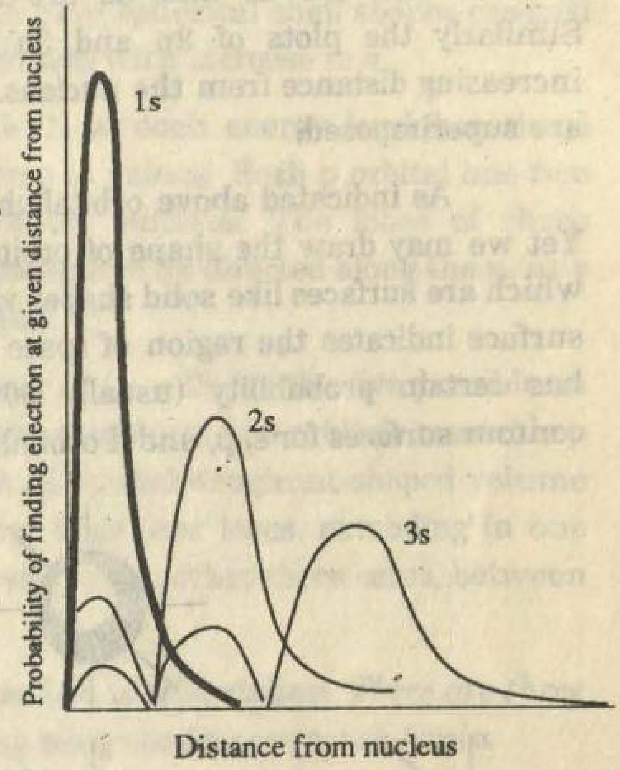
n	*l*	*m*	*ms*	*Number of Electrons in Subgroup*		*Electron State*
1	0	0	± ½	2	2	s
2	0	0	± ½	2	8	s
	1	1	± ½			
		0	± ½	6		p
		−1	± ½			
3	0	0	± ½	2	18	s
	1	1	± ½			
		0	± ½	6		p
		−1	± ½			
	2	2	± ½			
		1	± ½			
		0	± ½	10		d
		−1	± ½			
		−2	± ½			
4	0	0	± ½	2	32	s
	1	1	± ½			
		0	± ½	6		p
		−1	± ½			
	2	2	± ½			
		1	± ½			
		0	± ½	10		d
		−1	± ½			
		−2	± ½			
	3	3	± ½			
		2	± ½			
		1	± ½			
		0	± ½			
		−1	± ½	14		*f*
		−2	± ½			
		−3	± ½			

4.16 Shapes of the Orbitals

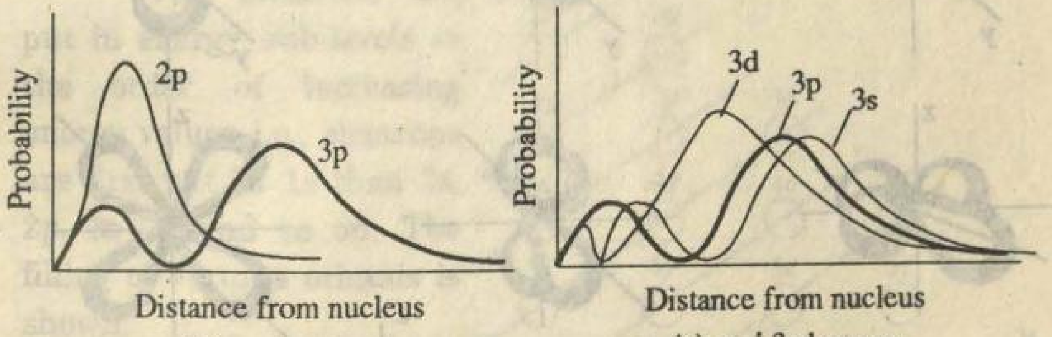
The term orbital in quantum mechanics refers to the wave function Ψ a solution of the Schrodinger equation. The wave function Ψ gives the amplitude of the standing wave

corresponding to the electron in a particular quantum state, while its square is the probability of finding the electron at some point in space.

The shapes of the orbitals have no physical existence. The shapes of orbital are only regions in space within which electrons can be found with certain probability. But these regions have no boundaries. One way of picturing the orbitals is to look at the relative locations of electrons in the principal quantum levels.



(a) s electron



(b) p electrons

(c) n = 3 electrons

Fig. 4.20 — Relative locations of electrons. Probabilities of finding s, p and d electrons at relative distance from the nucleus.

An orbital with l = 0 is called an s orbital. A plot of the of the probability of finding 1s, 2s and 3s (where 1, 2, 3, represent the values n of the electrons) electrons at any distance

from the nucleus is shown in Fig. 4.20. From these plots it is easily seen that 1s is most likely to be found nearest to the nucleus and the 2s and 3s are successively farther away. Similarly the plots of 2p and 3p electrons show the same increasing distance from the nucleus. The plots of 3s, 3p and 3d are superimposed.

As indicated above orbitals have no sharpe boundaries. Yet we may draw the shape of orbitals as probability contours which are surfaces like solid shapes viewed from a distance. The surface indicates the region of space within which the electron has certain probability (usually 90%) of being found. Such contour surfaces for s, p, and d orbitals are shown in Fig.4.21.

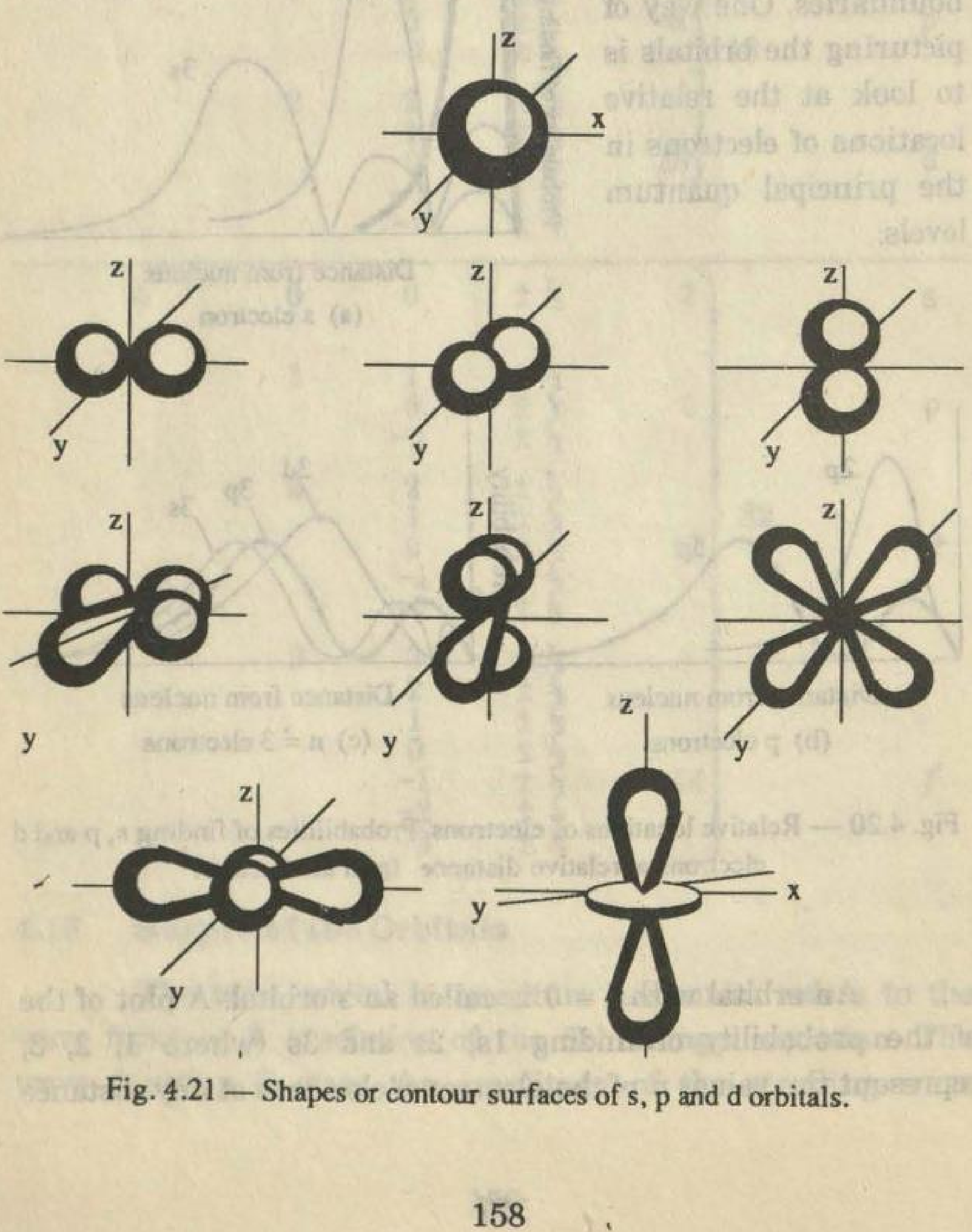


Fig. 4.21 — Shapes or contour surfaces of s, p and d orbitals.

A group of orbitals with the same energy (i.e., with the same values of n) is referred to a *sub shell*, while a group of sub shells with similar energies (same value of n) form a shell.

All s orbitals (l = 0) have spherical shell shapes centred at the nucleus. The size increases with increase in *n*.

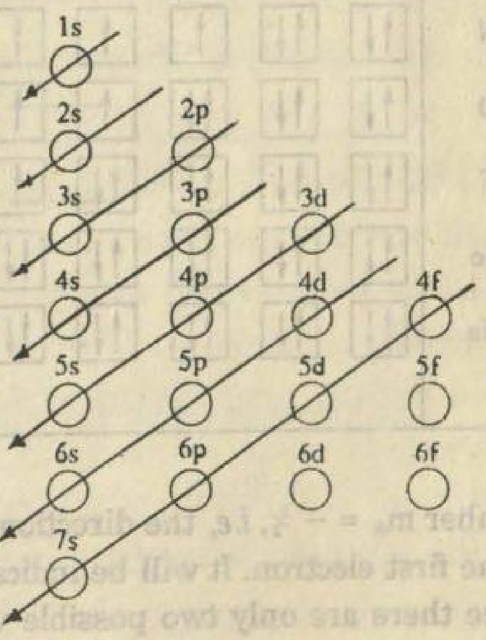
The p sub-shell (l= 1) at each energy level has three different orbitals for the three m values Each p orbital has two lobes one on each side of the nucleus. The lobes of three different p orbitals can be thought of as directed along the x, or y or z axis of a set of coordinates.

There are five d orbitals (l = 2) for the five possible m values. Their shapes are more complex and d orbitals resemble p orbital along z-axis with an additional doughunt-shaped volume in the center. The other four have four lobes, extending in one case along the x and y axis and in the other three cases, between the axis (xy, yz, zx).

4.17 Rules for Distribution of Electrons. *There are three rules for distributing electrons in energy sub-levels.*

(i) Auf-Bau Principle

The electrons are put in energy sub-levels in the order of increasing energy values i.e., electrons are first put in 1s then 2s, 2p, 3s .... and so on. The filling of various orbitals is shown.



(ii) Pauli Exclusion Principle

According to this principle "no two electrons in an atom can have the same set of four quantum numbers". For example,

take the case of the electron in 1s orbital. For this electron n = 1, l = 0 and m = 0. Suppose the electron under consideration has m_s = + 1/2. This may be indicated by an upward arrow (↑). Now if another electron is put in the same orbital (1s) its n = 1, l = 0, m = 0. It can occupy this orbital only if its spin quantum

Table 4.5

Element	Orbital electron structure						Linear expression of electron structure
	1s	2s	$2p_x$	$2p_y$	$2p_x$	3s	
H	↑						$1s^1$
He	↑↓						$1s^2$
Li	↑↓	↑	□	□	□		$1s^2 2s^1$
Be	↑↓	↑↓	□	□	□		$1s^2 2s^2$
B	↑↓	↑↓	↑	□	□		$1s^2 2s^2 2p_x^1$
C	↑↓	↑↓	↑	↑	□		$1s^2 2s^2 2p_x^1\ 2p_y^1$
N	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p_x^1\ 2p_y^1\ 2p_z^1$
O	↑↓	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p_x^2\ 2p_y^1\ 2p_z^1$
F	↑↓	↑↓	↑↓	↑↓	↑		$1s^2 2s^2 2p_x^2\ 2p_y^2\ 2p_z^1$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p_x^2\ 2p_y^2\ 2p_z^2$
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^1$

number $m_s = -\frac{1}{2}$, *i.e*, the direction of its spin is opposite to that of the first electron. It will be indicated by downward arrow (↓). Since there are only two possible values of m_s, one orbital can contain a maximum of two electrons and only when the directions of the spin of one is opposed to that of the other. Two such electrons in the same orbital and having opposite spins are said to be paired and are written as (↑↓). An orbital while

occupied by an electron pair is called completely filled orbital. The maximum number of electrons in the various energy levels permitted by the Pauli exclusion principle is given in the Table 4.5. For learning complete electronic configuration, consult appendix-2

(ii) Hund's Rule

If we have degenerate orbitals (orbitals of same energy) available, and more than one electrons are to be placed in them they should be placed in separate orbitals with same spin, rather than putting in the same orbital with opposite spins.

Let us apply Hund's rule to carbon atom and then to nitrogen atom. The pairing of electrons starts when all the three P_x, P_y and P_z orbitals are first filled up with single electron as is the case with O, F and Ne atoms shown above in Table 4.5.

4.18 Energy Levels of Orbitals

The energies of orbitals in atoms having more than one electrons are illustrated in Fig. 4.22

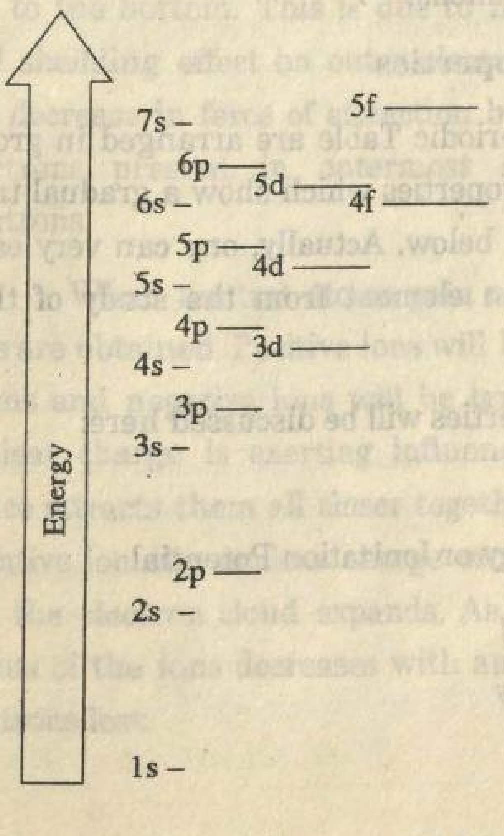


Fig. 4.22 — Electronic energy-level diagram for atomic orbitals.

These energy levels are arranged according to (n + l) rule. Both principal and azimuthal quantum numbers jointly decide about the position of sub-shell from nucleus. They are arranged with increasing (n + l) values. If (n + l) is same for more than one sub-shell, then small principle quantum number is to be filled earlier.

For the purpose of simplicity, we have indicated each orbital by means of a dash as it is composed of only one orbital. Likewise p, d and f sub-shells are shown as three, five and seven dashes respectively to indicate number of orbitals in each sub-shell. Note that each orbital of a given sub-shell has the same energy. Also note that as n becomes larger, the spacing between successive shells become less. Because of this narrowing energy separation, we begin to observe overlap among the sub-shells of third and higher sub-shells. The 4s sub-shell for example lies lower in energy than does the 3d sub-shell. This overlap is even more pronounced in higher shells.

4.19 Periodicity of Properties

The elements of Periodic Table are arranged in groups and periods. Some of the properties which show a gradual trend in their variation are given below. Actually, one can very easily predict the behaviour of an element from the study of these periodic properties.

The following properties will be discussed here:

(i) Size of Atoms

(ii) Ionization Energy or Ionization Potential

(iii) Electron Affinity

(iv) Electronegativity

4.20 Size of Atoms

The sizes of atoms are expressed in terms of atomic radii, ionic radii, covalent radii, and van der Waals radii. We shall give a brief description of some of them.

4.20.1 Atomic and Ionic Radii

We know that electron behaves like a wave. Due to this nature of electron, an atom does not have strictly defined boundaries. Hence it is not possible to determine its absolute dimensions. Generally, we deal with the radii of atoms linked together by some type of chemical bond.

The atomic radii of elements vary periodically throughout the Periodic Table of elements. Within the period, the radii decrease as the charge on the nucleus increases. The greatest decrease from left to right is observed in the elements of the short period because their outer shells are filled. In longer periods we observe smooth reduction of radii within the families of d and f elements. The atomic radii increase in a group from top to the bottom. This is due to increase in number of shells and sheilding effect on outer electrons. Shielding effect means the decrease in force of attraction between the nucleus and the electrons present in outermost shell due to underlying electrons.

When neutral atoms gain or lose electrons completely, ions are obtained. Positive ions will be smaller than their parent atoms and negative ions will be larger. For a positive ion the nuclear charge is exerting influence on a few electrons and hence attracts them all closer together whereas in the case of a negative ion the nuclear charge must act upon more electrons and the electron cloud expands. As is shown in Table 4.6, the radius of the ions decreases with an increase in the number of electrons lost.

Table 4.6

Atomic and Ionic radii (in picometres) = 10^{-12}m

		Positive Ions		
		Atomic Radius	Ionic Radius	Charge
Group IA	Li	135	60	(+1)
	Na	154	95	(+1)
	K	196	133	(+1)
	Rb	211	148	(+1)
	Cs	225	169	(+1)
Group IIA	Be	90	31	(+2)
	Mg	130	65	(+2)
	Ca	174	99	(+2)
	Sr	192	113	(+2)
	Ba	198	135	(+2)
Group IIIA	Al	143	50	(+3)
	Ga	122	62	(+3)
	In	162	81	(+3)

		Negative Ions		
		Atomic Radius	Ionic Radius	Charge
Group VIIA	F	64	136	(−1)
	Cl	99	181	(−1)
	Br	114	195	(−1)
	I	133	216	(−1)
Group VIA	O	66	140	(−2)
	S	104	184	(−2)
	Se	117	198	(−2)
	Te	137	221	(−2)
Group VA	N	70	171	(−3)
	P	110	212	(−3)

Elements that form more than one ion

	Atomic Radius		Ionic Radius		Ionic Radius
Fe	126	Fe^{2+}	76	Fe^{3+}	64
Co	125	Co^{2+}	78	Co^{3+}	63
Cu	128	Cu^{+}	96	Cu^{2+}	72

4.20.2 Covalent Radii

The covalent radius of an atom is taken as one half distance between the nuclei of two like atoms forming a single covalent bond. Thus we can say that the bond distance between two atoms A and B should be the arithmetic mean of the bond lengths A-A. and B-B. For example C-C single bond has a value of 0.077nm. Similarly of Si-Si the covalent radius comes to be 0.118 nm. This works in simple diatomic molecules but this is not generally the case. The deviations can be attributed to many factors like multiple bonds, ionic character and various possible hybridised orbitals which determine the geometry of the covalently bonded molecules. The covalent radii are usually named according to the geometry of the molecule e.g., normal radii, tetrahedral radii, octahedral radii, square radii or metallic radii as the case may be. A comparison of the atomic radii and single bond covalent radii is shown in Table 4.7.

Table 4.7

Atomic and Covalent Radii (in nm)

Metals	Atomic radius	Single bond covalent radius	Non Metal	Atomic radius	Single bond covalent radius
K	0.227	0.202	C	0.077	0.0771
Ba	0.217	0.198	P	0.110	0.110
La	0.188	0.169	S	0.104	0.104
Pd	0.138	0.128	Br	0.114	0.114
In	0.162	0.149			

In the above table the discrepancies in the values of covalent radii are due to the difference in the electronegativities between the bonded atoms.

4.21 Ionization Energy or Ionization Potential

The ionization energy IE (sometimes called *ionizaion potential* IP) of an element is defined as the energy required or enthalpy change for the removal of the least tightly bound electron, from its isolated atom in the gaseous state. Ionization energies are given per mole of atoms or ions of a given type. For example,

$$1/2H_2 \longrightarrow H^+ + \bar{e}, \Delta H_0{}^0 = +1312 \text{ kJ/mol}$$

$$Mg \longrightarrow Mg^+ + \bar{e}, \Delta H_0{}^0 = +738 \text{ kJ/mol}$$

1312J is the *first ionization energy* of hydrogen and 738kJ is the IE of Mg. It is expressed in kJ/mol. The subscript zero in the energy notation indicates that the energy refers to the value determined at 0°C.

If second electron is ejected from the singly positive ion it is known as *second ionization energy*. For example,

$$Mg^+ \longrightarrow Mg^{2+} + \bar{e}, \Delta H_0{}^0 = +1451 \text{ kJ/mol}$$

The ejection of second and third electrons require greater energy to form + 2 and + 3 cations.

The ionization energy depends upon the following factors;

(*i*) The magnitude of the nuclear charge.

(*ii*) The distance of the outermost electron from the nucleus i.e., atomic radius

(*iii*) The shielding effect of the underlying shells of electrons.

(*iv*) The extent to which the outer electron penetrates the charged cloud set up by the low lying electrons.

In the Periodic Table, the ionization energy decreases down the groups. This decrease is rapid upto 4th period and

slight for 6th and 7th period. The ionization energy increase from left to right along a period. As the number of protons in the nucleus and the nuclear charge goes on increasing with an increase in the atomic number the attractive influence of the nucleus on the shells increases and the electrons become more tightly bound and difficult to remove. Thus energy required to eject an electron increases and there is an increase in the ionization energy from left to right. The periodicity of the ionization energy can be seen in the diagram between the first ionization potential and atomic number as shown in Table 4.8.

Table 4.8

First Ionization Energies (kJ/mol at 0K)

Ionization energies increase across periods →

Ionization energies decrease down groups ↓ ; Highest first ionization energy (Noble Gases)

Group I							Noble Gases
H 1312	Group II	Group III	Group IV	Group V	Group VI	Group VII	He 2372
Li 520	Be 899	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1521
K 419	Ca 590	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351

The values in this table must be converted to approximate values at 298 K by adding 6.91 kJ.

4.22 Electron Affinity

The electron affinity is defined as the minimum energy released when an electron is absorbed in the lowest energy state of an isolated atom in the gaseous state to form an anion. Electron affinity is also expressed in kJ/mol. For example.

$$Cl(g) + e^- \longrightarrow Cl^-(g) \quad \Delta H^0_0 = -348.8 \text{ kJ/mol}$$

When a second electron is absorbed in a uni-negative ion the incoming electron is repelled by the -ve ion and energy is absorbed in this process i.e, it is an endothermic process. For example,

$$O + e^- \longrightarrow O^-, \Delta H^o{}_0 = -141\ kJ/mol$$

But for O^{-2} its value is + 844 kJ/mol

The electron affinities of various elements are shown below in the Table 4.9.

Table 4.9

Electron Affinities (kJ/mol at 0K)

(Values in parentheses have been calculated from theory; others are from experimental measurements).

Group I							Noble Gases
H –73	Group II	Group III	Group IV	Group V	Group VI	Group VII	He (21)
Li 60	Be (240)	B – 83	C –123	N 0.0	O –141	F –322	Ne (29)
Na –53	Mg (230)	Al (–50)	Si –120	P –74	S – 200	Cl –349	Ar (35)
K – 48	Ca (156)	Ga (–36)	Ge –116	As –77	Se –195	Br –325	Kr (39)

It is also observed that E.A. decreases from lighter to heavier elements in a given group of the Periodic Table. This is quite clear in Cl, Br and I. The representative member of each period i.e., Li, Be, B, C, N, O and F have lower electron affinity than the next heavier members. It is because the incoming electrons are repelled by the electrons already present in the atom. This effect is unusually high for the smaller atoms in 2nd

period. Second and higher order of E.A. are all negative in sign because of the repulsion between the electrons being added and the negatively charged ion. Electron affinity cannot be measured easily by experiments, although it has been accomplished in a few cases. However, it is possible to arrive at electron affinities by indirect method based on other measurements.

4.23 Electronegativity

The measure of the ability of an atom to attract an electron pair to itself in a chemical bond is called electronegativity. When covalent bonds are formed by unlike atoms, they will have greater ability to attract electrons as compared to others. Electronegativity depends on the number of protons in a nucleus and size of the atom. Non-metals have greater electronegativities than metals.

Mullikan defined electronegativity as average of the ionization energy and electron affinity. Pauling assigned numbers on an arbitrary scale from 0 to 4 as a measure of electronegativities of atoms (Table 4.10)

Table 4.10

Electronegativities of the Representative Elements

Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII
H						
(2.1)						
Li	Be	B	C	N	O	F
(1.0)	(1.5)	(2.0)	(2.5)	(3.0)	(3.5)	(4.0)
Na	Mg	Al	Si	P	S	Cl
(0.9)	(1.2)	(1.5)	(1.8)	(2.1)	(2.5)	(3.0)
K	Ca					Br
(0.8)	(1.0)					(2.8)
Rb	Sr					I
(0.8)	(1.0)					(2.5)
Cs	Ba					At
(0.7)	(0.9)					(2.2)

Electronegtivity values are derived from experimental data on the basis of energy required to break the bonds between atoms. The covalent bond formed between two dissimilar atoms is polar in the sense that one end is negative and the other is positive.

In the Periodic Table, electronegtivity increases from left to right and decreases down a group. Thus the most electronegative atoms are the non-metals at the upper right of the Periodic Table. Fluorine is the most electronegative element (E.N. = 4.0) followed by oxygen (E.N. = 3.5) and chlorine (E.N. = 3.0)

Electronegativities depend on the following factors.

(*i*) Atomic size (*ii*) Nature of combining atoms (*iii*) Atomic number (*iv*) Atomic volume (*v*) Electron affinities (*vi*) Ionization energy.

Electronegtivity values help in deciding the nature of a bond in a molecule. If electronegativity difference is more than 1.7 the bond will be ionic in nature. If E.N. values are less than 1.7 covalent bond will be formed. The bond between Na(E.N. = 0.9) and Cl(E.N. = 3.0) in Na^+Cl^- is ionic because electronegtivity difference is 2.1. The bond between HCl shows covalent character because electronegtivity difference is 0.9 (E.N.of H = 2.1 and Cl = 3.0).

EXERCISE

1. What led to the discovery of electrons, protons, and neutrons? Give the characteristic properties of each.

2. Describe experiments to measure.

   (*i*) Charge of electron.

   (*ii*) e/m value of electron.

How can the mass of electron be calculated?

3. What are canal rays? How the discovery of protons can be concluded from discharge tube experiment? Give properties of canal rays.

4. What is radioactivity? Discuss the characteristic features of α, β and γ–rays.

5. How will you distinguish between natural and artificial radioactivity? Discuss with suitable examples.

6. How are X-rays produced? What information about atom could be obtained after the discovery of X-rays.

7. *(a)* Explain the term 'atomic number' with suitable examples.

   (b) How do the x-rays give the idea of atomic number?

8. What is Planck's quantum theory of radiations? Discuss relationship of frequency, wave length and wave number of radiations with energy of photon. Compare the energies of photons of various spectral regions in the continuous spectra.

9. *(a)* Explain the difference between continuous and line spectra.

   (b) What is the origin of line spectra?.

10. Explain Rutherfords model of atom. On which experiment was it based? Discuss some drawbacks of this model of atom.

11. Discuss in detail the various aspects of Bohr's model of atom. What is the usefulness of this concept?

12. Discuss some defects of Bohr's atomic model. How is this concept applied to explain the hydrogen spectrum?

13. *(a)* How can the spectral lines of H-atom be explained on the basis of Bohr's atomic model?

(b) Describe the essential features of Heisenberg's uncertainity principle.

14. Calculate the energies, frequencies and wave numbers of the photons of light having wave length 600nm, and 509 nm respectively.

$$h = 6.6262 \times 10^{-34} Js \qquad c = 3 \times 10^{8} ms^{-1}.$$

15. What energy, frequency, wave length and wave number is associated with a photon of radiation, when an electron jumps from n = 3 to n = 1 orbit in H - atom. In what region of spectrum does this radiation lie?

16. What are quantum numbers? What is the concept of quantum numbers based on? Discuss the significance of each quantum number.

17. Discuss the shapes of s and p orbitals. What is the significance of ψ^2? Draw orbital pictures of s,p and d orbitals.

18. *(a)* How do Pauli's exclusion principle and Hund's rule help us to fill electrons in energy sub-levels? Explain (n + *l*) rule and give its application.

(b) Distribute electrons in energy sub-levels and orbitals, for the following atoms.

Fe_{26}, La_{57}, K_{19}, Au_{79}, Br_{35}, As_{33}

19. What is ionization energy? On what factors does it depend? Discuss general trends of ionization energy in the Periodic Table.

20. Differentiate between ionization energy and electron affinity. How do they vary in the Periodic Table? What is the usefulness of determining these values?

21. Explain the following:

(a) Atomic Radii (b) Covalent Radii

(c) Ionic Radii (d) Van der Waal's Radii

(e) Electronegativity.

22. (a) Discuss the relative values of atomic and ionic radii in groups and periods.

(b) How do you differentiate between covalent radius and Van der Waal's radius of an atom?

23. Arrange the following elements:

(a) Increasing order of ionization potential;

(b) Decreasing order of electron affinities.

(c) Increasing order of electronegativities.

Mg, Al, Na, Ar, Cl, S, Si, Cs, I.

24. Fill in the blanks with suitable words given inside the brackets.

(i) ________ are positive while ________ are negatively charged (electrons/protons)

(ii) The mass of ________ is less than ________ (neutrons/proton).

(iii) Cathode rays travel in discharge tube from ________ towards ________ while canal rays travel towards ________ (cathode/anode).

(iv) Electrons bend towards ________ when allowed to pass through magnetic field (north pole/south pole/none of the poles).

(v) Nature of cathode rays is ________ for H_2, He and CO_2 gas (not same/same).

(vi) The charge of electron was determined by ________ and its e/m value by ________ (Thomson/Millikan/Crooks).

(vii) The charge on electron is ________ and it is ________ on proton (same as /different from / $1.6 \times 10^{-19}C^{-}/6.625 \times 10^{-19}$ C).

(viii) The e/m for cathode rays is always ________ than anode rays (less/greater).

(ix) α-rays are ________ energetic than β-rays (more/less).

(xi) An orbital can have maximum of ________ electron (2/6/10).

(xii) Gases become conductors of electricity at ________ pressure (low/high).

(xiii) Electron and photons behave ________ according to de-Broglie's idea (alike/not alike).

(xiv) Nucleus ________ disintegrated in natural and artificial radioactivity (is not/is).

(xv) Neutron was discovered by ________ (Stoney/Chadwick).

(xvi) Energy of a photon is ________ proportional to the frequency ________ proportional to wave length. (directly/inversly).

(xvii) Photons of red colour are ________ energetic than that of violet colour (more/less).

(xviii) The energy associated with the electron revolving around the nucleus of atom is less for ________ orbits (lower/higher).

(xix) The radius of H-atom ________ on the number of orbital (depends/does not depend).

(xx) The distances between adjacent energy levels in H-atom are ________ (constant/not constant).

(xxi) The electron in first energy level of an atom moves ________ than in second energy level (slower/faster).

(xxii) The energy gap between adjacent energy levels ________ in H-atoms (remain same/changes).

(xxiii) Layman series lies in ________ region, Balmer in ________ region (Visible/U.V).

(xxiv) Pauli's exclusion principle is applicable to ________ orbitals (degenerate/two electrons in the same).

(xxv) Electronegativity ________ from left to right and ________ from top to bottom in the Periodic Table (decrease/increase).

(xxvi) Energy is ________ in measuring Ionization energy of an element but is ________ in measuring Electron affinity (evolved/absorbed).

(xxvii) Second Ionization energy is ________ than first one (less/more).

5

CHEMICAL BONDING

5.1 Introduction

The attractive force that holds atoms together is called a **"chemical bond"**. The properties of a substance are determined in part by the chemical bonds that hold the atoms together. Atoms of elements other than noble gases do not have stable electronic configuration. They therefore, try to attain stable electronic configuration. The tendency of elements to attain the stable electronic configuration is the cause of chemical reactivity. A chemical reaction produces a change in electronic configuration. Only the electrons of outer most shell can take part in this change. These electrons are farthest from the nucleus, so they are loosely held and are readily available for chemical combination.

5.2 Energetics of Chemical Bond Formation

Every physical system has a tendency to go from a higher energy state to a lower energy state. When atoms combine to form molecules, they come close to one another and interact in such a way that the energy of the system is lowered. The process of bond formation involves forces of attraction between two atoms which result in the formation of a molecule and the energy of the system decreases. In order to explain the decrease in energy of the system in bond formation a graph is plotted between the potential energy of two atoms against the internuclear distance 'R' as shown in Fig. 5.1

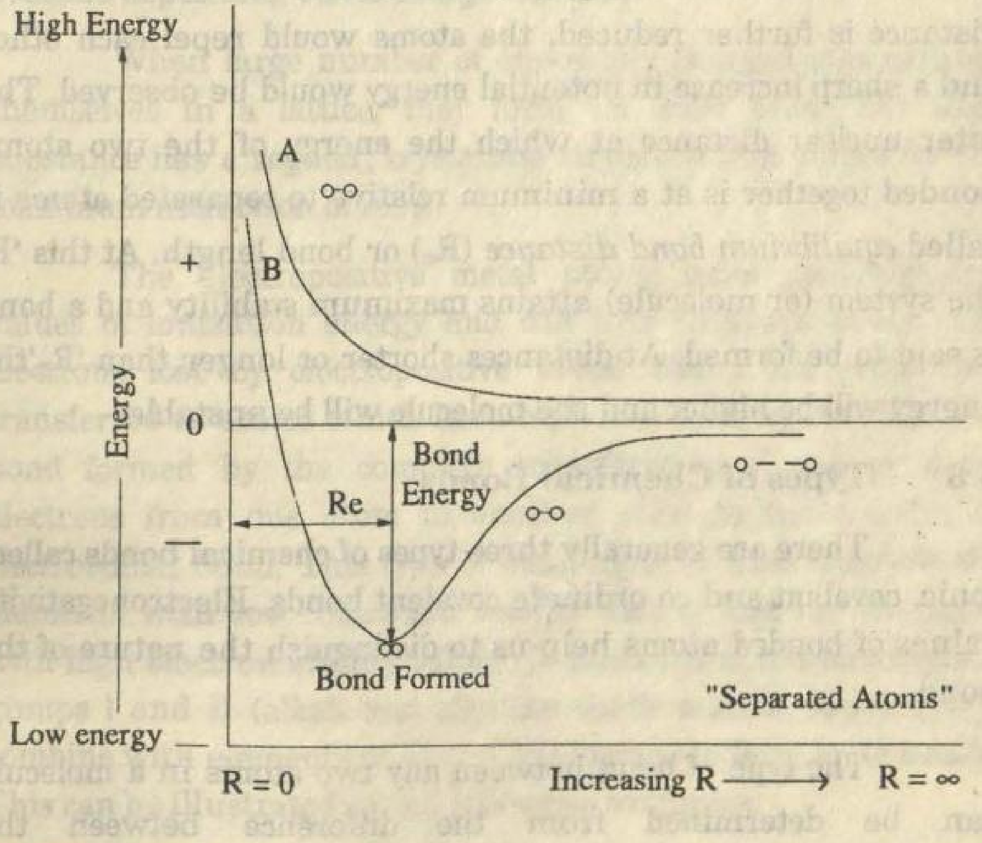


Fig. 5.1 — Plots of potential energy versus internuclear distance. Plot A indicates repulsive interaction. Potential energy of the system increases and no bond is formed. Plot B indicates an attractive interaction. Potential energy becomes minimum. Internuclear distance between atoms R_e is the equilibrium bond distance or bond lenght.

Let us consider what happens when two atoms approach each other. One possibility is that they repel each other. The repulsion increases with decrease of distance. This will result in

an increase in the potential energy of the system as shown by the curve A. The system will be unstable and no bond will be formed. The atoms will try to move away from each other toward an infinite separation to attain lower potential energy.

The other possibility is that the two atoms attract each other as shown by the curve B. The potential energy of the system composed of the two atoms will decrease with the decrease in the distance between them. At certain distance the energy of the two atoms will be at a minimum and a bond will be formed. The energy of the molecule, thus formed, will always be lower than the total energy of the separated atoms. If the bond distance is further reduced, the atoms would repel each other and a sharp increase in potential energy would be observed. The inter nuclear distance at which the energy of the two atoms bonded together is at a minimum relative to separated atoms is called *equilibrium bond distance* (R_e) or bond length. At this 'R' the system (or molecule) attains maximum stability and a bond is said to be formed. At distances shorter or longer than 'R_e'the energy will be higher and the molecule will be unstable.

5.3 Types of Chemical Bonds

There are generally three types of chemical bonds called, ionic, covalent and co-ordinate covalent bonds. Electronegativity values of bonded atoms help us to distinguish the nature of the bond.

The type of bond between any two atoms in a molecule can be determined from the difference between the electronegativity values of the two bonded atoms. If the difference is approximately 1.7, the bond has 50% ionic character and for a difference less than 1.7, the bond is necessarily a covalent bond. If electronegativity difference is greater than 1.7, the bond is ionic. The nature and formation of the three types of bonds is discussed as under. (See Table 5.1)

Table

5.4 Ionic or Electrovalent Bond

W. Kossel, a German chemist in 1916 suggested that an inert gas configuration could be attained by actual transfer of electrons from one atom to another. An ionic bond corresponds to the electrostatic attraction between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other. The atom that loses electrons becomes a cation (positive ion), and the atom that gains electrons becomes an anion (negative ion). Any given ion tends to attract as many neighbouring ions of opposite charge as possible depending on its charge and size.

When large number of oppositely charged ions arrange themselves in a lattice, they form an ionic solid. The ionic substance has a regular, crystalline structure that allows for the maximum attraction of ions.

The electropositive metal atoms have generally low values of ionization energy and can lose electrons easily. The electrons lost by electropositive metal atoms are completely transferred to atoms which have higher electronegativities. The bond formed by the complete transference of one or more electrons from one atom to another atom is called *ionic or electrovalent bond.* This type of bonding is formed between the elements with low ionization energy values and the elements with high electron affinity values. It means that the elements of groups I and II (alkali and alkaline earth metals, respectively) combine with elements of VI and VII groups to form ionic bonds. This can be illustrated by the following examples:

(i) Formation of Sodium Chloride

It is formed by the combination of sodium and chlorine atoms. The electronic configuration of sodium and chlorine atoms are:

$_{11}Na$ $\quad 1s^2, 2s^2, 2p^6, 3s^1$

$_{17}Cl$ $\quad 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

In order to attain the stable configuration of an inert gas the elements can undergo the following changes.

Sodium loses one electron to attain the electronic configuration of neon ($1s^2,2s^2,2p^6$).

$$\underset{(1s^2,2s^2,2p^6,3s^1)}{Na} \longrightarrow \underset{(1s^2,2s^2,2p^6)}{Na^+ + \bar{e}}$$

Chlorine gains one electron to acquire the electronic configuration of argon ($1s^2,2s^2,2p^6,3s^2,3p^6$).

$$\underset{(1s^2,2s^2,2p^6,3s^2,3p^5)}{Cl + \bar{e}} \longrightarrow \underset{(1s^2,2s^2,2p^6,3s^2,3p^6)}{Cl^-}$$

The oppositely charged ions formed in this way are held together by electrostatic forces of attractions.

$$\overset{+}{Na}_{(g)} + :\ddot{\underset{..}{Cl}}:^{-}_{(g)} \longrightarrow \overset{+}{Na}[:\ddot{\underset{..}{Cl}}:]^{-} \longrightarrow Na^+\,Cl^-_{(s)}$$

In order to understand the energy changes involved in the formation of sodium chloride the following steps should be considered.

The removal of an electron from the influence of the positively charged sodium nucleus requires energy, which is equal to 496kJ/mol.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + e^-, \Delta H = +496kJ/mol$$

(First ionization energy of Na)

The chlorine atom gains this electron to form a negatively charged ion (Cl^-) and its outer shell is filled, releasing 349kJ/mol.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \quad \Delta H = -349kJ/mol$$

(Electron affinity of Cl)

The formation of one mole of Na^+ and one mole of Cl^- from one mole each of Na and Cl would increase the energy of the system by (+ 496 −349) = 147kJ. As the energy of the system has increased, the transfer of electrons from sodium atoms to chlorine atoms cannot be responsible for the formation of bonds. However oppositely charged ions so produced attract each other and arrange themselves to form a crystal lattice of sodium chloride which consists of closely packed oppositely charged ions, each sodium ion surrounded by six chloride ions and each chloride ion surrounded by six sodium ions. The force of attraction between these oppositely charged ions in the lattice greatly decreases the energy of the system.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow Na^+\,Cl^-_{(s)},\ \Delta H = -\,787\text{kJ/mol}$$

The total decrease in the energy of the system in the formation of one mole NaCl from one mole each of Na and Cl atoms is (+496 −349 −787)kJ or −640kJ. Therefore the energy of $Na^+Cl^-_{(s)}$ is lesser than the total energy of separated atoms Na and Cl. Hence the ionic bond formed in Na^+Cl^- will be more stable.

Let us take another example to explain the ionic bonding.

(ii) Formation of Calcium Chloride

The calcium atom loses two electrons to form Ca^{2+} ions and acquires the electronic configuration of argon ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$). These two electrons are taken up by two chlorine atoms to form Cl^- ion.

$$Ca\ -2e^- \longrightarrow Ca^{2+}$$

$$(1s^2,2s^2,2p^6,3s^2,3p^6,4s^2). \qquad (1s^2,2s^2,2p^6,3s^2,3p^6)$$

$$2Cl\ +2e^- \longrightarrow 2Cl^-$$

$$(1s^2,2s^2,2p^6,3s^2,3p^5). \qquad (1s^2,2s^2,2p^6,3s^2,3p^6)$$

$$Ca \longrightarrow Ca^{++} + 2e^-$$

The ions so produced then pack themselves in a crystal lattice due to electrostatic forces of attraction with a huge decrease in the energy of the system.

$$Ca^{2+} \quad + \quad 2\,:\ddot{\underset{..}{Cl}}:^{-} \longrightarrow :\ddot{\underset{..}{Cl}}:^{-}\,Ca^{2+}\,:\ddot{\underset{..}{Cl}}:^{-} \longrightarrow CaCl_2$$

Consequently the ionic bonds formed between Ca^{2+} and $2Cl^-$ are very stable.

Characteristics of Ionic Compounds

- (*i*) Most of the ionic compounds are solid at room temperature.
- (*ii*) Ionic compounds have high melting and boiling points.
- (*iii*) Ionic compounds are soluble in polar solvents like water.
- (*iv*) The ionic compounds dissociate when dissolved in water and conduct electricity in molten or dissolved state.
- (*v*) The crystals of ionic compounds are made up of ions.
- (*vi*) The ionic bond is non-directional in character.
- (*vii*) The reaction between ionic compounds are usually very fast.

5.5 Covalent Bond

Transfer of electrons from the valence shell of one atom to the valence shell of another atom is not the only mode by which atoms attain stable configuration of noble gases and a lower energy state. Similar stable configuration can also be achieved by sharing electrons in the valence shells. For example two hydrogen atoms may share their single electron of the

valence shell with each other and attain the electronic configuration of noble gas, helium (He).

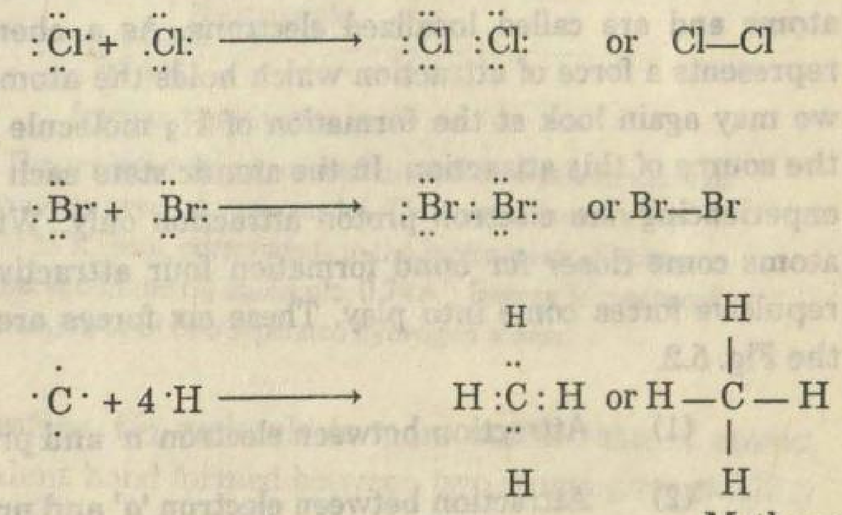
$$H^{\cdot} + {}^{\cdot}H \longrightarrow H:H \quad \Delta H^{o} = -435\ kJ/mol$$

A bond thus formed by the mutual sharing of electrons between two atoms is called a *covalent bond*. The covalently bonded atoms are at lower energy than the separated atoms. The atoms with low electronegativity differences usually form covalent bonds. A bond is said to be 100% covalent if it exists between atoms of same element.

The shared pair of electrons of the covalent bond is also represented by a line or dash. For example H_2 molecule is also represented as H—H. A dash represents one shared pair of electrons.

5.5.1 Single Bond

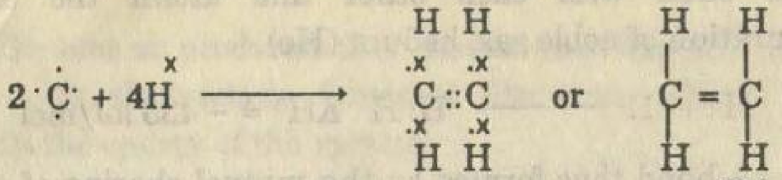
A single covalent bond is produced when one electron pair (two electrons) is shared between two atoms. It is represented by a single line, or a dash. For example:



Methane

5.5.2 Double Bond

A double covalent bond is that bond which is formed by sharing of two electron pairs (4 electrons) between two atoms and is denoted by two short lines, or dashes



Ethene

5.5.3 Triple Bond

A triple covalent bond is formed by sharing of three electron pairs (6 electrons) between two atoms and is represented by three short lines, e.g.

$$\cdot\dot{\underset{\cdot}{N}}: + :\dot{\underset{\cdot}{N}}\cdot \longrightarrow :N\vdots\vdots N: \quad \text{or} \quad N \equiv N$$

$$2\ \cdot\dot{\underset{\cdot}{C}}\cdot + 2\overset{\times}{H} \longrightarrow H\overset{\times}{\underset{\cdot}{}}C\vdots\vdots C\overset{\times}{\underset{\cdot}{}}H \quad \text{or H–C≡C–H}$$

Acetylene

5.5.4 Stability of a Covalent Bond

The shared pair of electrons in covalent bonds are restricted to the region between the two nuclei of the combining atoms and are called localized electrons. As a chemical bond represents a force of attraction which holds the atoms together, we may again look at the formation of H_2 molecule to identify the source of this attraction. In the atomic state each H· atom is experiencing one electron-proton attraction only. When two H atoms come closer for bond formation four attractive and two repulsive forces come into play. These six forces are shown in the Fig. 5.2.

(1) Attraction between electron '*a*' and proton 'A'

(2) Attraction between electron '*a*' and proton 'B'

(3) Attraction between electron '*b*' and proton 'A'

(4) Attraction between electron '*b*' and proton 'B'

(5) Repulsion between electron '*a*' and electron 'b'.

(6) Repulsion between proton 'A' and proton 'B'.

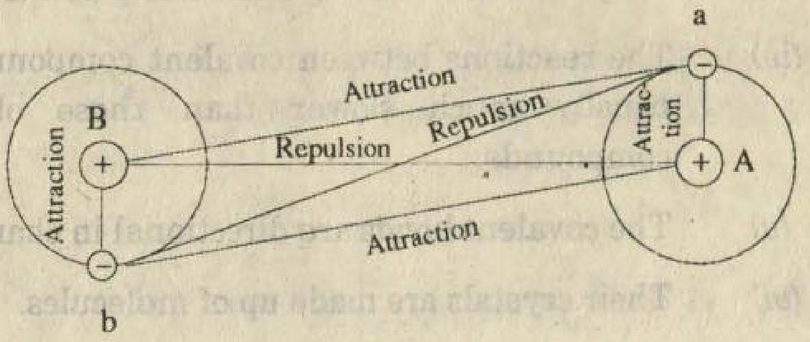


Fig. 5.2 — Attractive and repulsive forces between protons and electrons of two atoms of hydrogen.

The resultant of these six forces must be a net attractive force (Fig 5.2) because the formation of hydrogen molecules from atoms of hydrogen is exothermic and releases 435kJ/mole of energy (Fig.5.3).

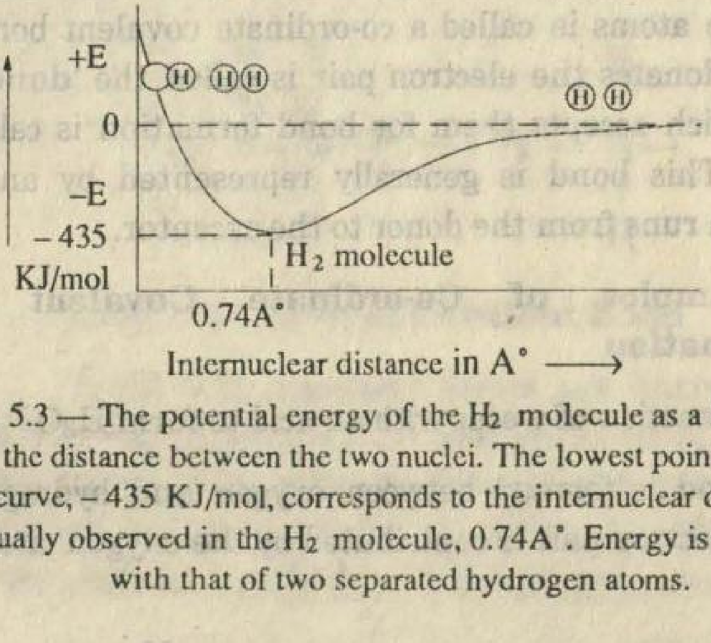


Fig. 5.3 — The potential energy of the H_2 molecule as a function of the distance between the two nuclei. The lowest point in the curve, – 435 KJ/mol, corresponds to the internuclear distance actually observed in the H_2 molecule, 0.74A°. Energy is compared with that of two separated hydrogen atoms.

Therefore, H_2 molecule is more stable than H atoms. Hence a covalent bond formed between two atoms gives stability to the molecule.

5.5.5 Characteristics of Covalent Compounds

(i) Covalent compounds are generally soluble in non-polar solvents.

(ii) They are bad conductors of electricity in molten state or in solutions in non polar solvents.

(iii) They have low melting and boiling points.

(iv) The reactions between covalent compounds are usually much slower than those of ionic compounds.

(v) The covalent bonds are directional in character.

(vi) Their crystals are made up of molecules.

5.6 Co-ordinate Covalent Bond

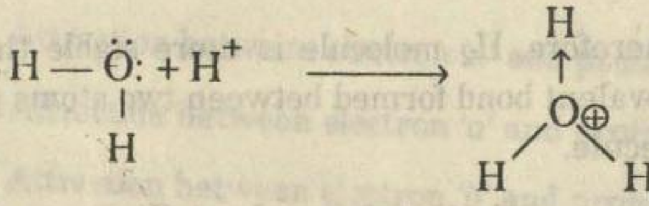
In the formation of a simple covalent bond each atom contributes one electron to the shared electron pair. But there are some cases in which only one of the two bonded atoms contributes the shared electron pair.

A covalent bond in which both the electrons are donated by one of the atoms is called a co-ordinate covalent bond. The atom which donates the electron pair is called the '**donor**' and the atom which accepts them for bond formation is called the '**acceptor**'. This bond is generally represented by an arrow (⟶) which runs from the donor to the acceptor.

Some Examples of Co-ordinate Covalent Bond Formation

(i) Reaction of water with an acid to form H_3O^+ ion.

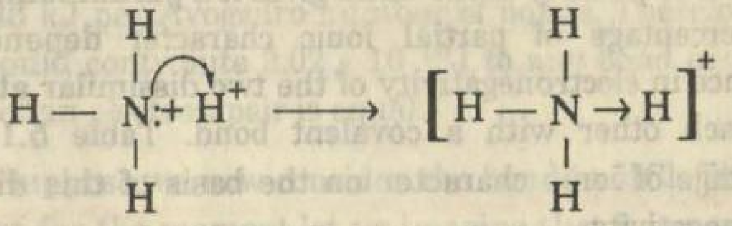
A bond is formed between oxygen and hydrogen ion. The shared electron pair is contributed by the oxygen atom.



Hydronium ion

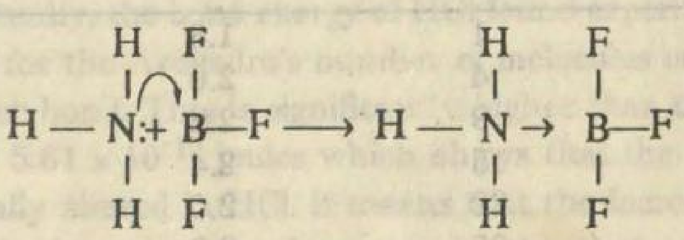
(ii) Reaction of ammonia with a proton (H^+) to give NH_4^+ ion:

A bond is established between the nitrogen and proton (H^+) by the donation of an electron pair from the nitrogen atom.



(iii) **Reaction of ammonia with boron trifluoride**

A bond is formed between the nitrogen atom and the boron atom and the shared electron pair has been contributed by the nitrogen atom.



5.7 Ionic Character of Covalent Bond

When two dissimilar atoms are linked by a covalent bond the shared electrons are not attracted equally by the two bonded atoms. Due to the unsymmetrical distribution of electron clouds one end of the molecule acquires partial positive charge and the other end acquires a partial negative charge.

For example, in case of HCl molecule, the electronegativity of Cl is 3.0 and the electronegativity of H is 2.1. Due to difference of E.N. values, the ability of chlorine atom to attract the shared pair of electrons is greater than that of hydrogen atom. The covalent bond between H and Cl acquires a partial ionic character as shown below:

$$\overset{\delta^+}{H} — \overset{\delta^-}{Cl}$$

Such bonds are called polar covalent bonds. One end of polar covalent bond acquires a partial negative charge and the

other end a partial positive charge. On the other hand non-polar Cl—Cl covalent bond carries symmetrical concentration of electronic charge in the space between the two atoms.

The polarity of the bond gives it a partial ionic character. The percentage of partial ionic character depends on the difference in electronegativity of the two dissimilar atoms joined with each other with a covalent bond. Table 5.1 gives the percentage of ionic character on the basis of this difference of electronegativity.

Table 5.1

Ionic character of Bonds

Electro negativity difference	Percent ionic Character	Electro negativity difference	Percent ionic Character
0.2	1	1.8	55
0.4	4	2.0	63
0.6	9	2.2	70
0.8	15	2.4	76
1.0	22	2.6	82
1.2	30	2.8	86
1.4	39	3.0	89
1.6	47	3.2	92
1.7	51		

5.8 Bond Energy

The strength of a bond can be determined by measuring the energy required to break the bond in a molecule. It is therefore defined as the energy required to break one mole of bonds to form neutral atoms. The bond energy of a polar molecule is greater than that of a non-polar molecule.

The relation between bond energy and electronegativity can be seen from the following examples.

It is found that 435kJ of energy is required to break the bonds between one mole of H_2 into individual atoms. Thus, the bond energy of H_2 molecule is 435 kJ per Avogadro number of

bonds or 7.22×10^{-19}J per bond. Because the sharing of electron pair is equal between the two H atoms, it would be reasonable to assume that each bonded atom contributes half the bond energy or 3.61×10^{-19}J per bond. Similarly, the bond energy found for Cl_2 is 243 kJ per Avogadro number of bonds. Therefore, one Cl atom should contribute 2.02×10^{-19}J to any bond in which the sharing of an electron pair is equal.

Suppose we now consider the bond in HCl. This bond is polar, but for the moment let us imagine that it is non-polar i.e. the electron pair is shared equally. It means the H in HCl to be the same as in H_2 and Cl to be the same as in Cl_2.If H contributes 3.61×10^{-19}J and Cl 2.02×10^{-19}J the expected bond energy of HCl should be the sum of these values or 5.63×10^{-19} joules which indicates that the electrons are equally shared in HCl. Actually, the bond energy of HCl found experimently is 431 k joules for the Avogadro's number of molecules or 7.15×10^{-19} joules per bond. This is significantly higher than the calculated value of 5.61×10^{-19} joules which shows that the electrons are not equally shared in HCl. It means that the increased stability of HCl is due to unequal sharing of the electron pair which results in further lowering of the energy. Thus H and Cl are more strongly bound and the difference in the calculated and experimental bond energy is an additional binding energy. The amount of additional binding energy would depend on the relative pulling ability of electrons of the bonded atoms, since the greater the charge difference between the end of the molecule, the greater the additional binding energy. When the bond energies of the hydrogen halides (HX) are compared with the value calculated by assuming equal sharing of electrons, the discrepancy is the greatest in the HF and least in HI. This means that the sharing of electrons between H and F is more unequal than the sharing between H and I. The electronegativity values assigned to F(4.0), Cl (3.0), Br (2.8), I (2.5) and H(2.1) are consistent with the trend towards equal sharing. It shows that in HF the sharing of electrons is most unequal and in HI it is the

least. This is also supported by their dipole moments; HF, 1.94D; HCl, 1.08D; H Br, 0.78D; and HI, 0.38D.

The decreasing polarity indicates a trend towards equal sharing of electrons in hydrogen halides. It means that the order of decreasing bond energies in hydrogen halides would be HF > HCl > HBr > HI.

5.9 Dipole Moment

A diatomic molecule with a polar bond is a dipole. Whether or not a molecule is a dipole depends not only upon bond polarity but also upon molecular geometry and the presence of lone-pair electrons.

Dipole moment is measured experimentally by placing the sample of a substance in an electric field and noting the decrease in the magnitude of an initially applied electric field (Fig 5.4). From this decrease and the use of calculations

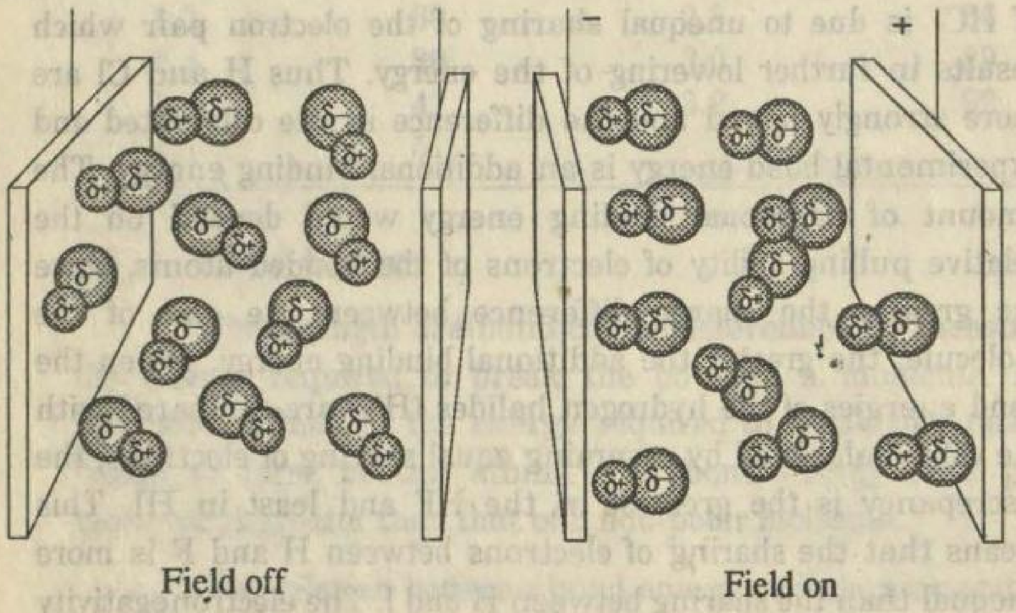


Fig. 5.4 — In an electric field polar molecules tend to lineup in an electric field, pointing their negative ends toward the positive plate and their possitive ends toward the negative plate. This lining up of the molecules tends to neutralize and thereby decrease the magnitude of an initially applied electric field. Non polar molecules are not affected.

developed by Peter Debye, dipole moment can be evaluated. The degree of polarity of a molecule is expressed in terms of its dipole moment μ, (Greek letter mu). Dipole moment is a measure of the separation of charge in a molecule. It is the product of charge times the distance that separates it from a charge of equal magnitude but opposite sign as:

dipole moment = charge x distance

$\mu = d \times e$

In SI units dipole moments μ are measured in Coulomb - meter (C.m.) However commonly used unit is debye D.

$D = 3.34 \times 10^{-30}$ C.m.

The shape of a molecule can be related to whether or not it has a dipole moment. A triatomic or more complex molecule may or may not have a dipole moment depending upon the geometric arrangement of polar bonds. This is because dipole moment is the vector sum or resultant of bond moments. If the vector sum of bond moments is zero, the dipole moment will be zero and the molecule will be non polar. For example the dipole moment of CO_2 is zero although the molecule has polar bonds. This suggests a linear structure for CO_2 molecules.

The effect of one dipole just cancels the effect of the other. When a carbon dioxide molecule is placed in an electric field, there is no tendency for the molecule to turn. CS_2 molecule also balances like CO_2.

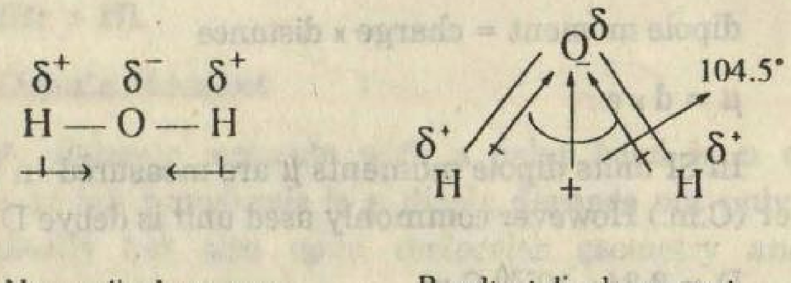
$$\overset{\delta^-}{S} = \overset{\delta^+}{C} = \overset{\delta^-}{S} \qquad \overset{-\delta}{O} = \overset{+\delta}{C} = \overset{-\delta}{O}$$

$$\longleftarrow \quad \longrightarrow \qquad \longleftarrow \quad \longrightarrow$$

In case of sulphur dioxide SO_2 one might expect a linear structure like CO_2. But SO_2 has a dipole moment of 1.62 D, which shows that bond moments do not cancel and the molecular geometry is angular.

Water H_2O is a triatomic molecule in which two hydrogen atoms are bonded to the same oxygen atom. There are

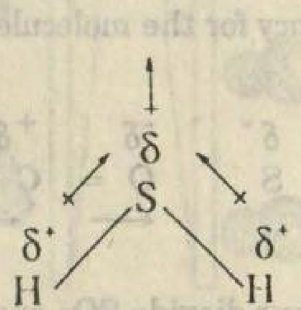
two different possibilities for its structure. The structure may be linear with the three atoms arranged in a straight line or the atoms may be arranged in the form of a bent chain. The two possibilities are shown in Fig. 5.5(a) and (b)



No net dipole moment Resultant dipole moment

(a) Fig. 5.5 (b)

The experimental fact that water has a very high dipole moment of 1.84 D supports the bent structure (b). The linear structure (a) would represent a non-polar molecule in which two polar bonds would be placed in line so that there would be no net dipole moment. Actually in molecule of water the two bond dipoles do not cancel out but owing to the bent structure, gives a resultant moment as shown in Fig. 5.5(b). A similar behaviour is also shown by H_2S molecule which has a dipole moment $\mu = 0.92$ D.



Triangular molecule of BF_3, tetrahedral CH_4 and CCl_4 have zero, dipole moments. Fig. 5.6.(a – c) The resultant dipole moments cancel the effect of each other. But NH_3 has a dipole moment because it is pyramidal molecule Fig. 5.6(d).

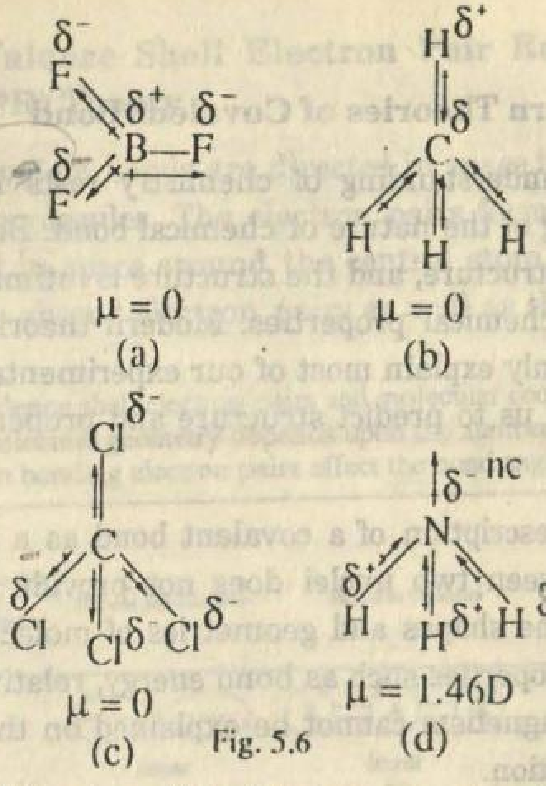


Fig. 5.6

Table 5.2 gives the dipole moment values of some molecules and their geometrical shapes.

Table 5.2

Dipole Moments and Shapes of Molecules

Molecule	Dipole moment	Shape of molecule	Molecule	Dipole moment	Shape of molecule
HF	1.78	Linear	NH_3	1.46	Pyramidal
HCl	1.03	Linear	PH_3	0.55	Pyramidal
HBr	0.78	Linear	BF_3	0	Trigonal planar
HI	0.38	Linear	SO_3	1.86	Trigonal planar
CO	0.12	Linear	CH_3Cl	1.86	Tetrahedral
H_2O	1.84	angular	CH_2Cl_2	1.59	Tetrahedral
CO_2	1.63	angular	$CHCl_3$	1.03	Tetrahedral
H_2S	0.95	angular	CCl_4	0	Tetrahedral
CO_2	0	Linear	CH_4	0	Tetrahedral
CS_2	0	Linear			

5.10 Modern Theories of Covalent Bond

The understanding of chemistry rests heavily on the understanding of the nature of chemical bond. Bonding is a key to molecular structure, and the structure is intimately related to physical and chemical properties. Modern theories of chemical bonding not only explain most of our experimental observations but also allow us to predict structure and properties to a great extent.

The description of a covalent bond as a shared pair of electrons between two nuclei does not provide much help in determining the shapes and geometries of molecules. Similarly many other properties such as bond energy, relative strengths of bonds, paramagnetism cannot be explained on the basis of this simple description.

Presently three theories are being used to understand the nature of covalent bond. The first is the Valence Shell Electron Pair Repulsion (VSEPR) theory. The basic assumption is that electron pairs are arranged around the central atom of a molecule in such a way that there is maximum separation (and therefore minimum repulsion among electron pairs). This idea is very useful in predicting the geometries of molecules and ions.

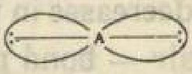
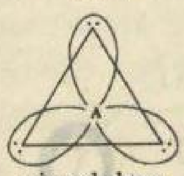
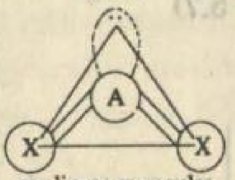
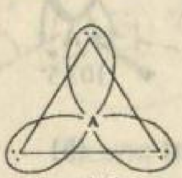
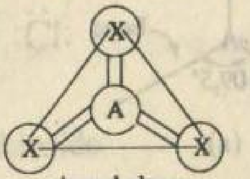
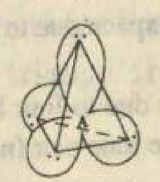
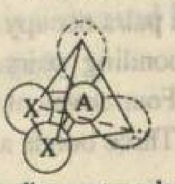
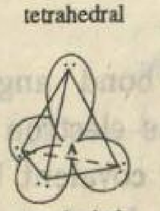
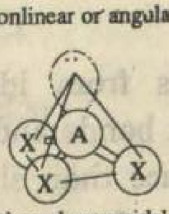
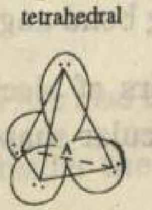
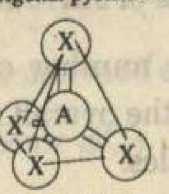
The second theory is the Valence Bond (VB) theory, which explains the bonding in terms of overlapping of atomic orbitals. This theory also allows mixing of atomic orbitals to form new orbitals with different spatial orientation. This mixing is called hybridization.

The third theory is the Molecular Orbital (MO) theory which explains bond formation as the occupation of orbitals characteristic of bonded atoms rather than individual atoms. Whereas VSEPR theory is exceedingly simple, the VB and MO theories require an intensive knowledge of quantum mechanics and make use of the methods of wave functions and orbital descriptions. We will however use a non- mathematical approach to describe VB and MO theories.

5.11 The Valence Shell Electron Pair Repulsion (VSEPR) Theory

The covalent bonds are directed in space to give definite shapes to the molecules. The electron pairs forming the bonds are distributed in space around the central atom along definite directions. The shared electron pairs as well as the lone pair of

Table 5.3 — Valence shell electron pairs and molecular geometry. Note that molecular geometry depends upon the number of bonds. Non bonding electron pairs affect the bond angle.

Total Number of Electron Pairs in valance shell	Number of Nonbonding Elecctron Pairs	Number of Bonds	Electron pair Geometry	Molecular Geometry	Formula
2	0	2	 linear	linear	$BeCl_2$, $MgCl_2$, $HgCl_2$
3	1	2	 trigonal planar	 nonlinear or angular	SO_2
3	0	3	 trigonal planar	 trigonal planar	BF_3, BCl_3
4	2	2	 tetrahedral	 nonlinear or angular	$H_2\ddot{O}$, $H_2\ddot{S}$
4	1	3	 tetrahedral	 trigonal pyramidal	NH_3, PH_3, AsH_3 etc
4	0	4	 tetrahedral	 tetrahedral	CH_4, CCl_4, SiH_4

electrons are responsible for the shape of molecules. Sidgwick and Powell (1940) pointed out that the shapes of the molecules could be explained on the basis of electron pairs present in the outer most shell (highest value of n) of the central atom. Pairs of electrons around the central atom are arranged in space in such a way so that the distances between them are maximum and coulombic repulsions of electronic clouds are minimized. Arrangement of electron pairs which lead to minimum repulsion are shown in Table. 5.3.

The known geometries of many molecules based upon measurement of bond angles show that lone pairs of electrons occupy more space than bonding pairs. The repulsion between electronic pairs in valence shell, decreases in the following order, Lone pair — lone pair > lone pair — bond pair > bond pair — bond pair. (Fig. 5.7)

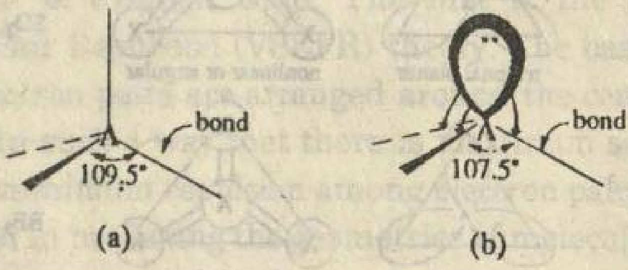


Fig. 5.7 — Lone pairs occupy more space due to greater repulsion than bonding pairs.
(a) Four covalent bonds due to four bond pairs.
(b) Three bonds and one lone pair (non-bonding pair).

Variations from ideal bond angles are caused by multiple covalent bonds and lone electron pairs both of which require more space than single covalent bonds and therefore cause compression of surrounding bond angles.

Thus the number of pairs of electrons in the valence shell determines the overall molecular shape. Let us explain this with some examples.

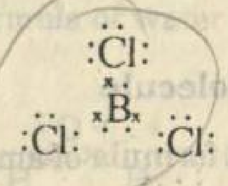
5.11.1 Shapes of Molecules Containing Two Electron Pairs

The two bond pairs of electrons in $BeCl_2$ arrange themselves as far apart as possible in order to minimize the repulsion between them. The only arrangement which can be given to satisfy this condition is linear.

:— Be —:	180^0 Cl--- Be---Cl
Bond Pairs in valence Shell of Be	Linear $BeCl_2$ Molecule

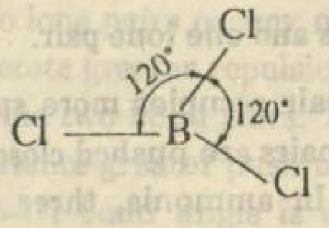
5.11.2 Shapes of Molecules Containing Three Electron Pairs

The electron dot structure of BCl_3 can be represented as



Boron trichloride

Thus there are three bond pairs around boron. It should, therefore, be a planar triangular molecule.



This structure has also been confirmed experimently.

Now let us consider the molecule SO_2. The electron dot structure of SO_2 is,

$$:\ddot{O} \leftarrow :\ddot{S} :: \ddot{O}:$$

The molecule has one double bond. Both pairs of electrons in a double bond must be confined to the same general region in the valence shell of an atom otherwise, it would not be a double bond. Therefore, a group of four electrons in a double bond behaves much like a group of two electrons in a single bond or a bond pair. The molecule also has one single bond and a lone pair on the central S atom. The molecule must therefore be non-linear. As the lone pair occupies more space, it will push the two bond pairs closer to each other, and the angle between two bond pairs becomes less than 120^{0}.

511.3 Shapes of Molecules Containing four Electron pairs

The electrostatic repulsion between four pairs of electrons is minimum when they are present at the corners of a regular tetrahedron. The angles between tetrahedrally arranged bonds are $109^{0}.5$

Shape of Ammonia Molecule

The electron dot formula of ammonia is

$$\begin{array}{c} \times\times \\ H \overset{\times}{\bullet} N \overset{\times}{\bullet} H \\ \bullet\times \\ H \end{array}$$

It has three bond pairs and one lone pair.

As the lone pair occupies more space than bond pairs, the three N--H bond pairs are pushed closer and the bond angle decreases to 107.5^{o}. In ammonia, three electrons of N atom combines with three electrons of H atoms and fourth vertex of N is occupied by the lone pair, giving it trigonal pyramidal structure as shown in Fig.5.8. The electronic configuration of N

in ammonia is tetrahedral, but the overall geometry is trigonal pyramid.

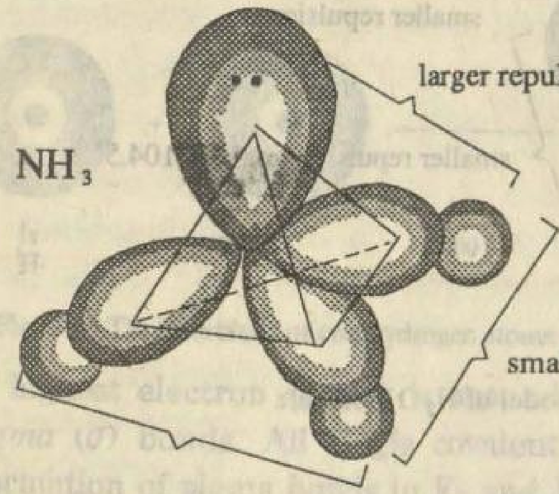


Fig. 5.8 VSEPR model of NH_3 molecule

Shape of Water Molecule

The electron dot formula of water molecule is as follows.

There are four electron pairs around oxygen atom, two lone pairs and two bond pairs. These four electron pairs are arranged towards the corners of a regular tetrahedron. The two corners are occupied by the two lone pairs and the other two corners by two bond pairs. The two lone pairs occupy more space than the two bond pairs and generate greater repulsion not only between themselves but also on the two bond pairs. Thus the two O—H bonds in H_2O will experience greater push than N—H bonds in NH_3. Hence the H—O—H bond angle is expected to deviate from the tetrahedral angle to a greater extent than the H—N—H angle in NH_3. The shape of water molecule becomes angular and the bond angle H—O—H is reduced to 104.5° as shown in Fig.5.9.

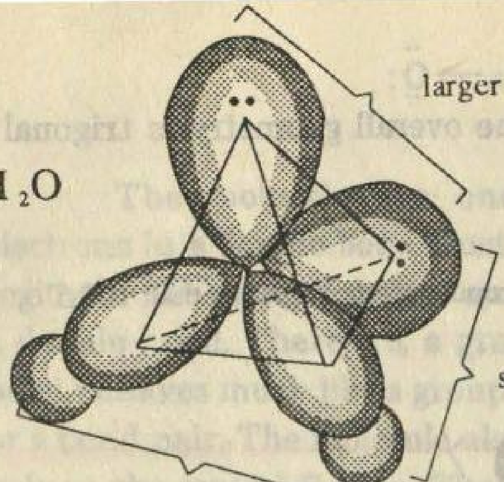


Fig. 5.9 VSEPR model of H_2O molecule

5.12 Valence Bond (VB) Theory of Covalent Bond

The VSEPR theory is quite successful in explaining and predicting molecular geometry, but fails to answer the basic questions. How do atoms share electrons in their valence shell and how do electrons due to their repulsion avoid each other. In order to find answers to these questions we look at the results of quantum mechanics. One approach to answer these questions is the valence bond (VB) theory.

The valence bond theory assumes that a covalent bond is formed by pairing of electrons by the overlap of orbitals of two atoms. Two orbitals each containing one electron (half filled) would overlap to form a single covalent bond. By overlap we mean that the electrons of overlaping orbitals share a common region of high electron density along *the line between two nuclei called bond axis.*

Now let us study some examples of bond formation as explained by VB theory.

5.12.1 Sigma Bond

The simplest example of bond formation by overlap of atomic orbitals is given by hydrogen molecule. Each hydrogen

atom has a half filled 1s atomic orbital. Overlap of two 1s orbitals allows pairing of electrons and the formation of a single covalent bond as shown in Fig.5.10. All such bonds in which region

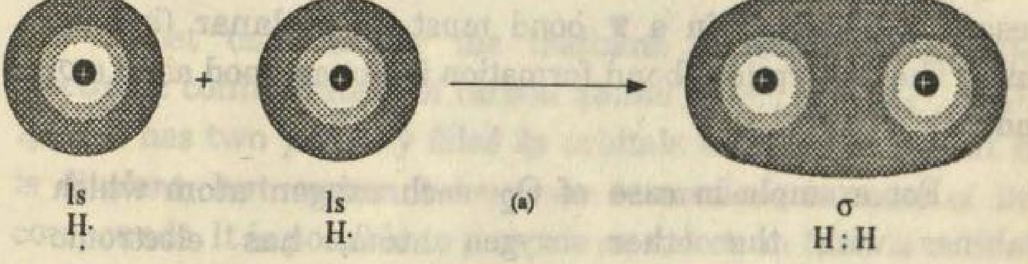


Fig. 5.10 The is orbitals of two hydrogen atoms overlap to form an s–s σ bond.

of highest electron density is around the bond axis are called *sigma* (σ) bonds. All single covalent bonds are sigma bonds. Formation of sigma bonds in F_2 and HF molecules is shown in Fig. 5.11.

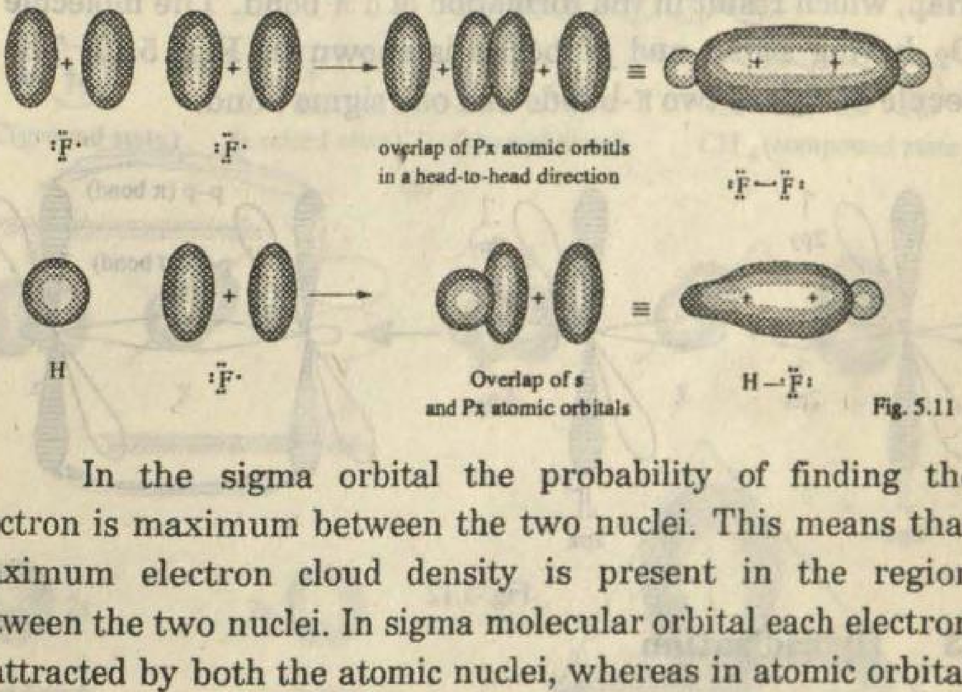


Fig. 5.11

In the sigma orbital the probability of finding the electron is maximum between the two nuclei. This means that maximum electron cloud density is present in the region between the two nuclei. In sigma molecular orbital each electron is attracted by both the atomic nuclei, whereas in atomic orbital it is attracted by only one nucleus. The increased attraction between nuclei and electrons lowers the energy of the system. Thus 435 kJ/mol energy is given out when two atoms combine to form a hydrogen molecule.

5.12.2 Pi(π) Bond

The bond which is formed due to the sidewise or parallel overlap of p orbitals of the two already bonded atoms is known

as Pi (π) bond. As given above p_x orbitals with axial overlap will form σ bond. But p_y and p_z orbitals will undergo parallel or lateral overlap and would result in the formation of π– bonds. These two p-orbitals in a π bond must be coplanar (in one plane). The overlap in π bond formation is not as good as in a σ bond.

For example in case of O_2, each oxygen atom which combines with the other oxygen atom, has electronic configuration $1s^2$, $2s^2$, $2p^1{}_x$, $2p^1{}_y$, $2p^2{}_z$. Thus there are two partially filled p orbitals on each oxygen atom. The two oxygen atoms are joined by two bonds. One of them is formed by axial overlap of $2p_x$ orbitals and forms a σ bond. The $2p_y$ orbitals of the two oxygen atoms further interact through parallel or lateral overlap, which result in the formation of a π bond. The molecule of O_2 having sigma and pi bonds is shown in Fig. 5.12. The molecule of N_2 has two π-bonds and one sigma bond.

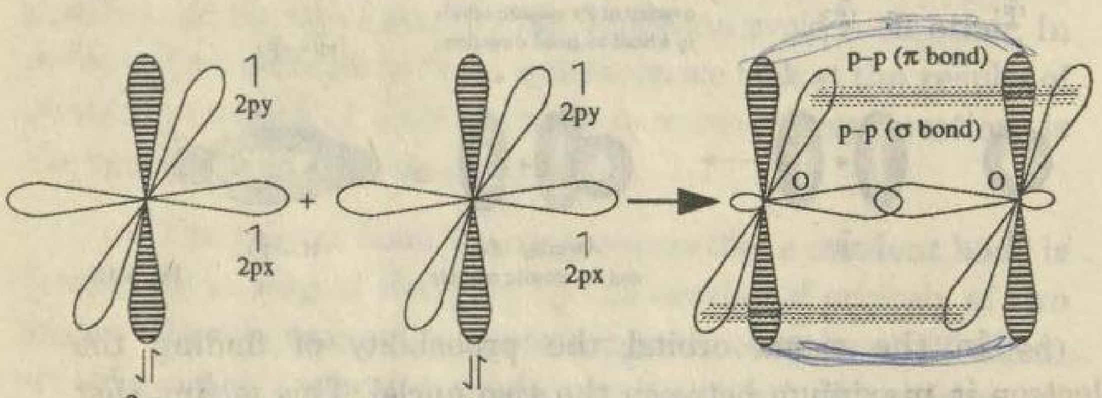


Fig. 5.12

5.13 Hybridization

It may be defined as a process in which *atomic orbitals of different energy and shape are mixed together to form a new set of equivalent orbitals of the same energy and same shape.* There are many different types of orbital hybridization but we will discuss here some very common types of hybridization.

5.13.1 sp^3-Hybridization

The mixing of one *s* and three *p* orbitals to form four equivalent sp^3 hybrid orbitals is called sp^3 hybridization. Each

sp^3 orbital has 25% *s*-character and 75% *p*-character. These sp^3 orbitals are directed from the centre of a regular tetrahedron to its four corners. The angles between tetrahedrally arranged orbitals are 109.5°.

Let us consider the methane molecule, CH_4. The electronic configuration of carbon atoms is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p^0_z$. It has two partially filled $2p$ orbitals which indicate that it is divalent, but carbon behaves as tetravalent in most of its compounds. It is possible to promote one electron from $2s$ orbital to an empty $2p_z$ and mixing of one *s* and three *p* orbitals give rise to four equivalent sp^3 hybridized orbitals (Fig. 5.13).

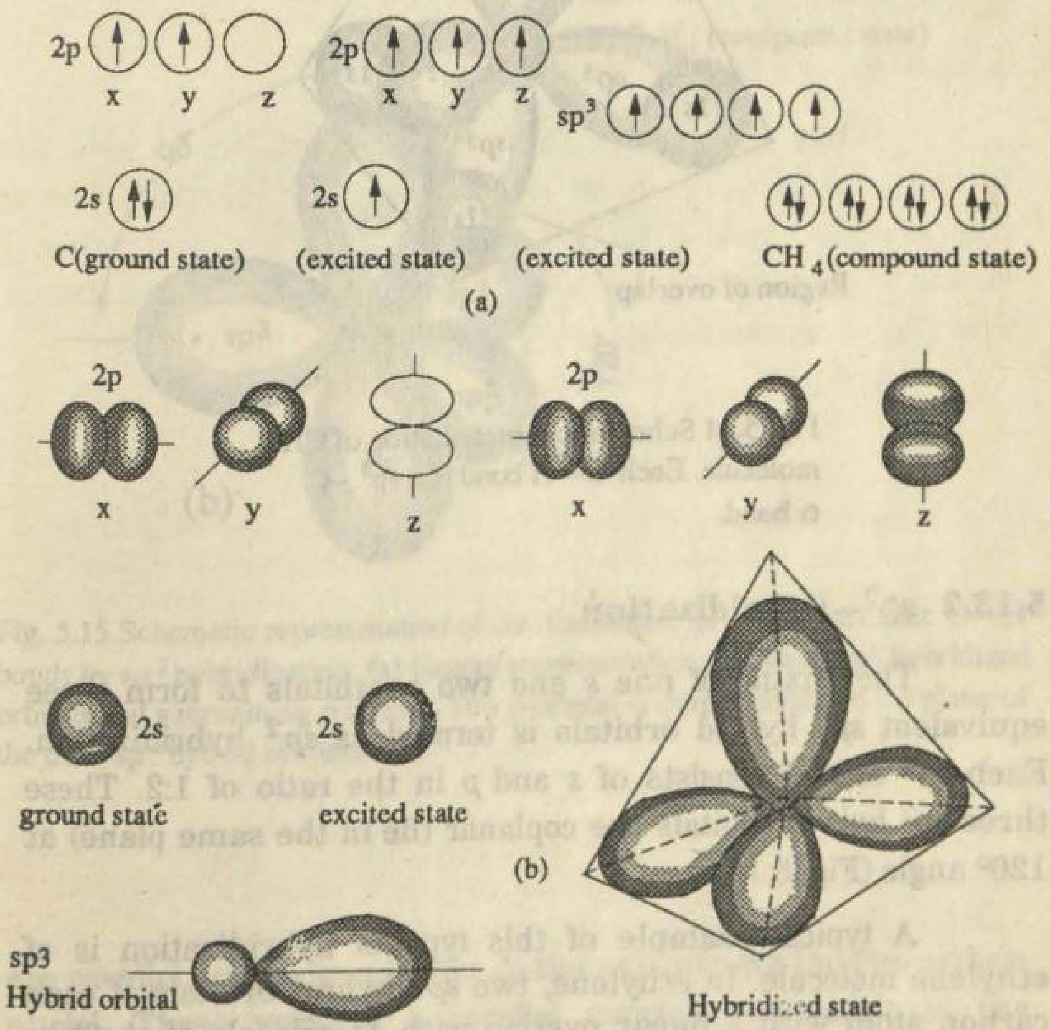


Fig. 5.13 Schematic representation of the formation of four equivalent C—H bonds by sp^3 hybridization. (a) Energy representation (b) Orbital representation of hybridized state.

The four sp^3 hybrid orbitals of the carbon atom overlap with $1s$ orbitals of four hydrogen atoms to form a methane molecule which contains four σ bonds (each due to sp^3-s overlap) and each H—C—H bond angle is 109.5° as shown in Fig. 5.14.

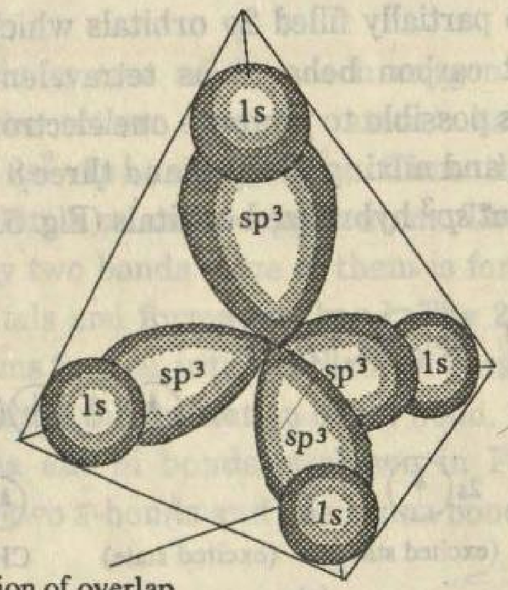


Fig. 5.14 Schematic representation of CH_4 molecule. Each C—H bond is a sp^3 –s σ bond.

5.13.2 sp^2—Hybridization

The mixing of one *s* and two *p* orbitals to form three equivalent sp^2 hybrid orbitals is termed as sp^2 hybridization. Each sp^2 orbital consists of *s* and *p* in the ratio of 1:2. These three sp^2 hybrid orbitals are coplanar (lie in the same plane) at 120° angle (Fig. 5.15)

A typical example of this type of hybridization is of ethylene molecule. In ethylene, two sp^2 hybrid orbitals of each carbon atom with a linear overlap with 1*s* orbitals of the two hydrogen atoms form two σ bonds, while the remaining sp^2 orbital on each carbon atom overlap axially to form a σ bond. The remaining two unhybridized *p* orbitals on two carbon atoms

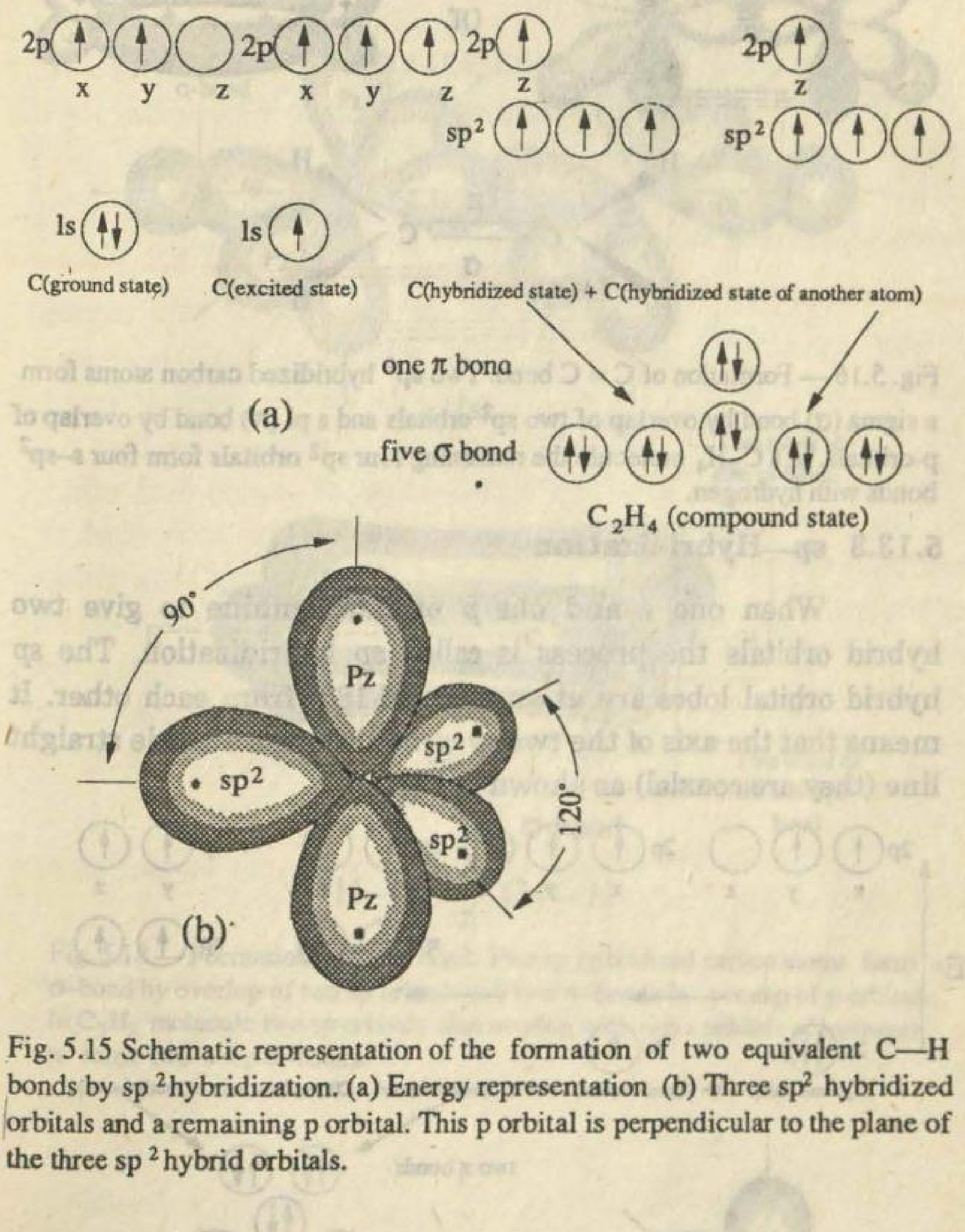


Fig. 5.15 Schematic representation of the formation of two equivalent C—H bonds by sp^2 hybridization. (a) Energy representation (b) Three sp^2 hybridized orbitals and a remaining p orbital. This p orbital is perpendicular to the plane of the three sp^2 hybrid orbitals.

are parallel and perpendicular to the axis joining the two carbon nuclei. These undergo a parallel overlap and result in the formation of a π orbital. Thus a molecule of ethylene contains five σ bonds and one π bond as shown in Fig. 5.16

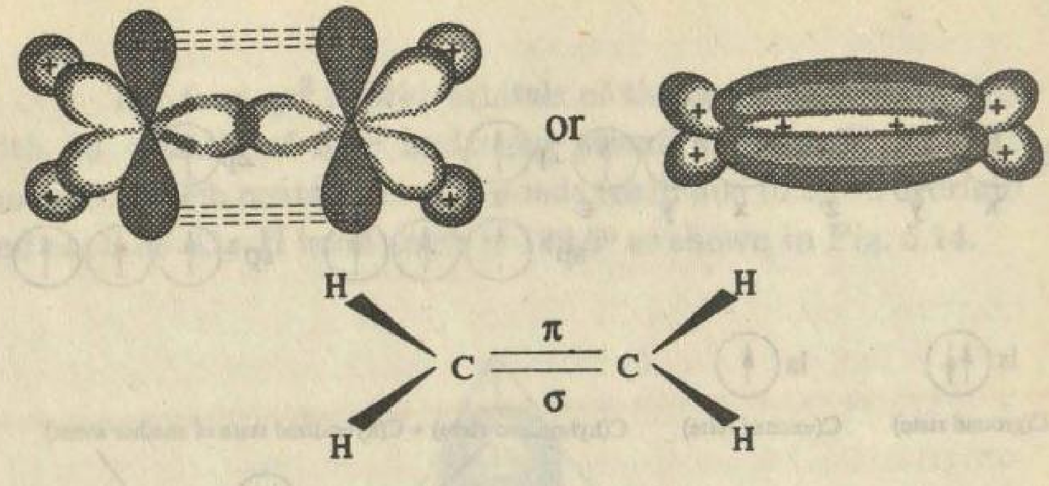
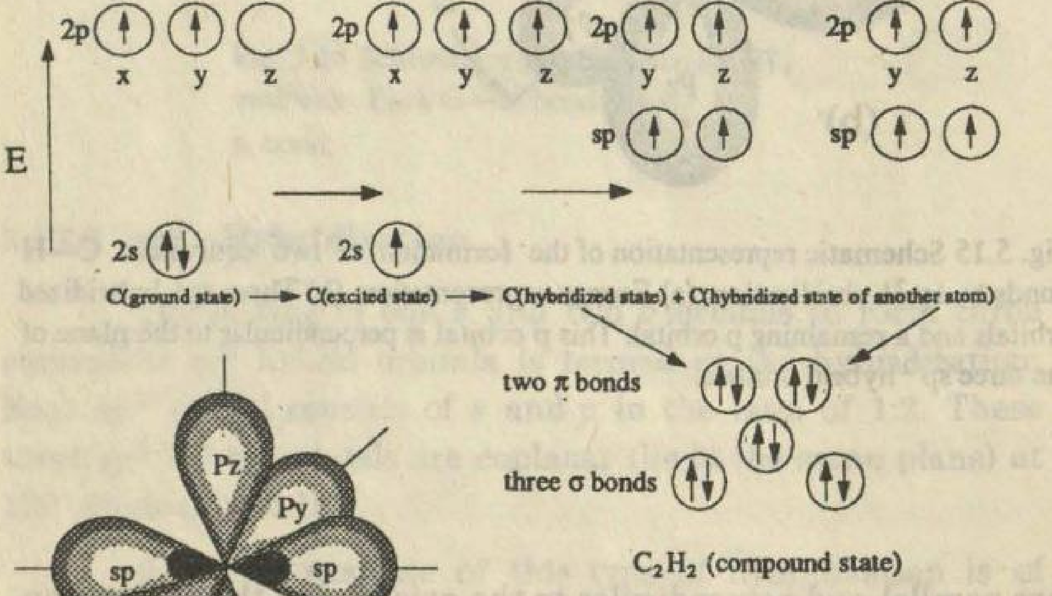


Fig. 5.16 — Formation of C = C bond. Two sp^2 hybridized carbon atoms form a sigma (σ) bond by overlap of two sp^2 orbitals and a pi (π) bond by overlap of p-orbitals. In a C_2H_4 molecule the remaining four sp^2 orbitals form four $s\text{–}sp^2$ bonds with hydrogen.

5.13.3 sp—Hybridization

When one *s* and one *p* orbital combine to give two hybrid orbitals the process is called *sp* hybridization. The *sp* hybrid orbital lobes are at an angle of 180° from each other. It means that the axis of the two *sp*–orbitals forms a single straight line (they are coaxial) as shown in Fig. 5.17.



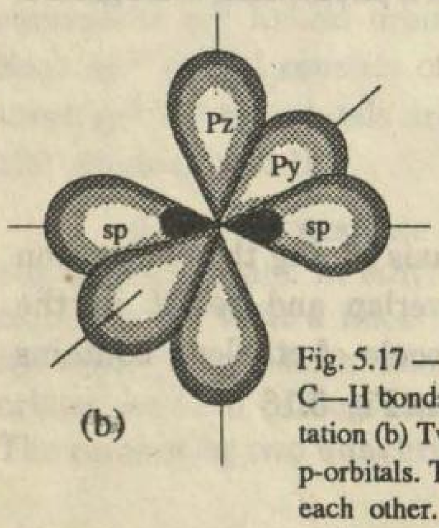


Fig. 5.17 — Schematic representation of two equivalent C—H bonds by sp hybridization. (a) Energy representation (b) Two sp hybridized orbitals and two remaining p-orbitals. Two sp hybridized orbitals are at 180° angle to each other. The p-orbitals are at 90° angle to each other and to sp orbitals.

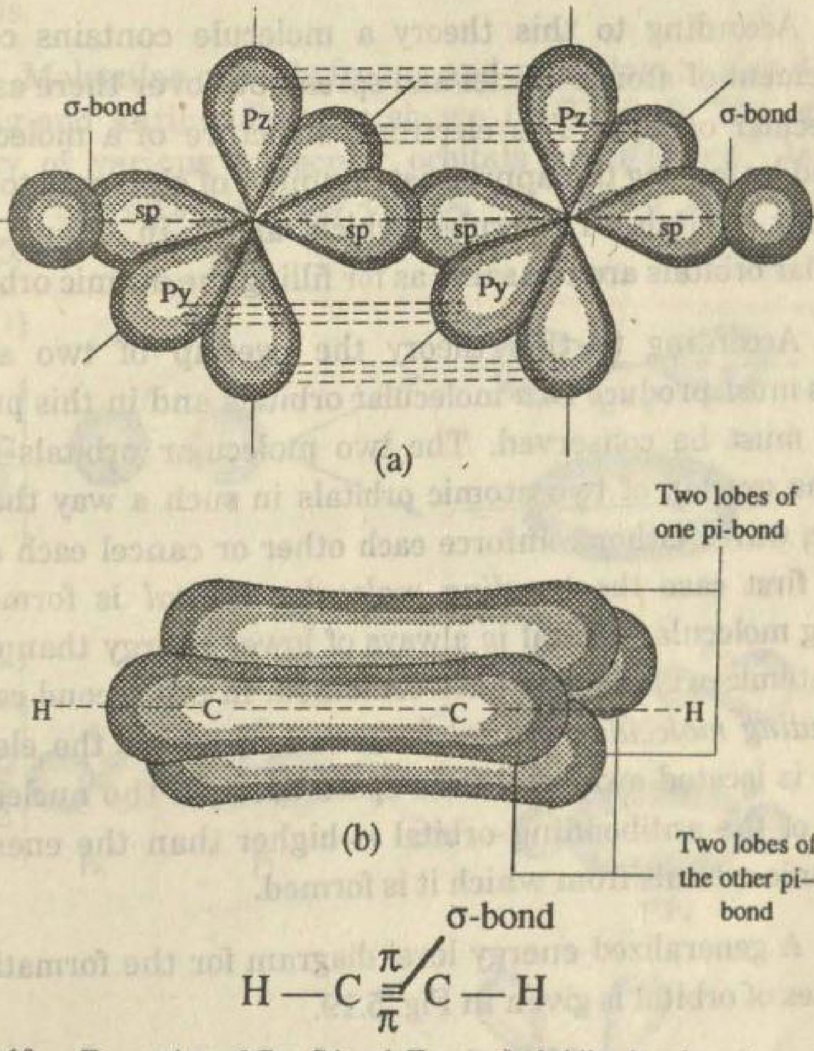


Fig. 5.18 — Formation of C ≡ C bond. Two sp hybridized carbon atoms form a σ–bond by overlap of two sp orbitals and two π–bonds by overlap of p-orbitals. In C_2H_2 molecule two sp orbitals also overlap with two s orbitals of hydrogen to form two s–sp σ–bonds.

In acetylene, the two sp hybridized orbitals of two carbon atoms linearly overlap and form a σ bond between them. The $2p_y$ and $2p_z$ unhybridized orbitals are perpendicular to each other and to a line through the centres of two sp hybrid orbitals. They overlap to form the π-bonds between two carbon atoms (Fig. 5.18).

5.14 Molecular Orbital (MO) Theory

According to this theory a molecule contains certain arrangement of atomic nuclei and spread out over there as a set of molecular orbitals. The electronic structure of a molecule is obtained by feeding the appropriate number of electrons to these molecular orbitals. The rules which apply in filling these molecular orbitals are the same as for filling the atomic orbitals.

According to this theory the overlap of two atomic orbitals must produce two molecular orbitals and in this process energy must be conserved. The two molecular orbitals result from the overlap of two atomic orbitals in such a way that the electron waves either reinforce each other or cancel each other. In the first case the *bonding molecular orbital* is formed. A bonding molecular orbital is always of lower energy than either of the atomic orbitals that have combined. In the second case an *antibonding molecular orbital* is formed in which the electron density is located away from the space between the nuclei. The energy of the antibonding orbital is higher than the energy of the atomic orbitals from which it is formed.

A generalized energy level diagram for the formation of two types of orbital is given in Fig. 5.19.

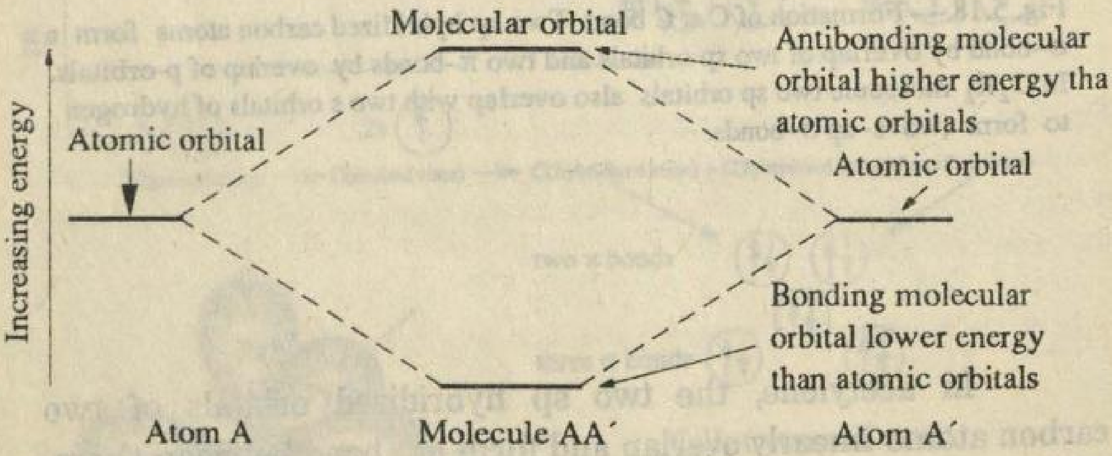


Fig. 5.19 — Energy levels of bonding and anti-bonding orbitals.

As in case of VB theory σ and π notations are used in MO theory as well. However antibonding molecular orbitals are

indicated by adding a star to the bonding molecular orbital symbols.

Molecular orbitals from *s* and *p* orbitals to give σ and π bonding and antibonding are shown in Fig 5.19. The order of stability of various molecular orbitals are $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$ and shown in Fig 5.20)

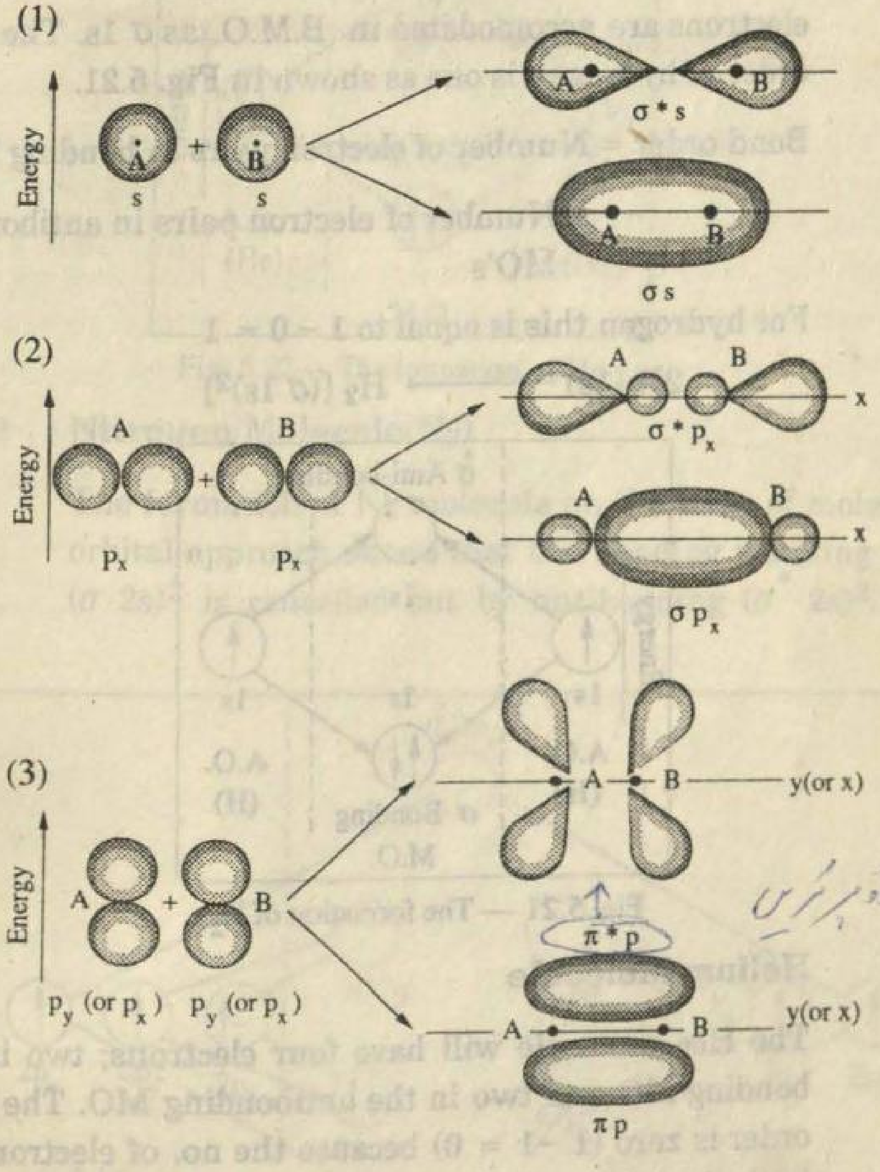


Fig. 5.20 — Representation of two atomic s & p orbitals to form σ & σ*, π & π* molecular orbitals.

The $\pi 2p_y$ and $\pi 2p_z$ bonding and antibonding molecular orbitals have the same energy, and are called degenerate orbitals. The Aufbau Principle, Pauli exclusion principle and

Hund's rule can now be applied to build up the electronic configuration of some simple homonuclear diatomic molecules.

5.14.1 Molecular orbital Treatment of some Homonuclear Diatomic Molecules

(i) H_2 Molecule

Two Is atomic orbitals of H having one electron in each generate two molecular orbitals σ 1s and σ^* 1s. Two electrons are accomodated in B.M.O. as σ 1s. The bond order of hydrogen is one as shown in Fig. 5.21.

Bond order = Number of electron pairs in bonding MO's

– Number of electron pairs in antibonding MO's

For hydrogen this is equal to 1 – 0 = 1

$$2H\ (1s) \longrightarrow H_2\ [(\sigma\ 1s)^2]$$

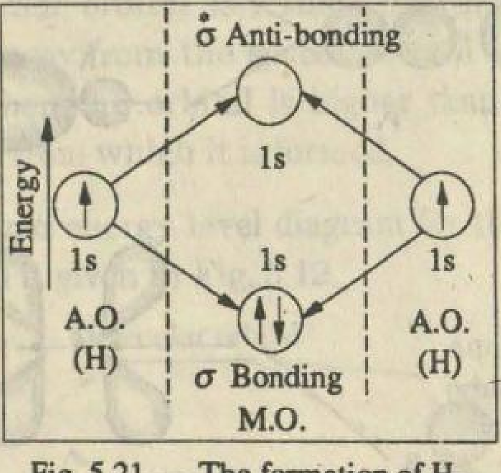


Fig. 5.21 — The formation of H_2.

(ii) Helium Molecule

The He_2 molecule will have four electrons; two in the bonding MO and two in the antibonding MO. The bond order is zero (1 –1 = 0) because the no. of electron pair in the bonding MO is eqaul to no. of electron pair in the antibonding MO. This molecule, therefore, does not exist under normal conditions. In order to explain this type of behaviour a general principle is observed that the

presence of equal number of electrons in the bonding and antibonding MO's leads to no bonding Fig. 5.22.

$$2He \xrightarrow{\times} He_2$$

$$2[1s^2] \qquad [(\sigma 1s^2)(\sigma^* 1s)^2]$$

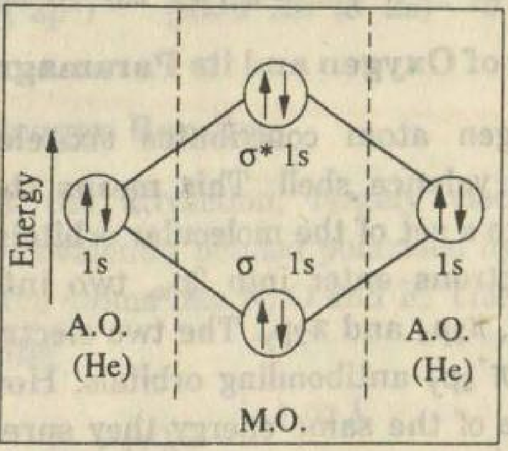


Fig. 5.22— The formation of He_2.

(iii) Nitrogen Molecule(N_2)

The formation of N_2 molecule on the basis of molecular orbital approach shows that the bonding resulting from $(\sigma\ 2s)^2$ is cancelled out by antibonding $(\sigma^*\ 2s)^2$. The

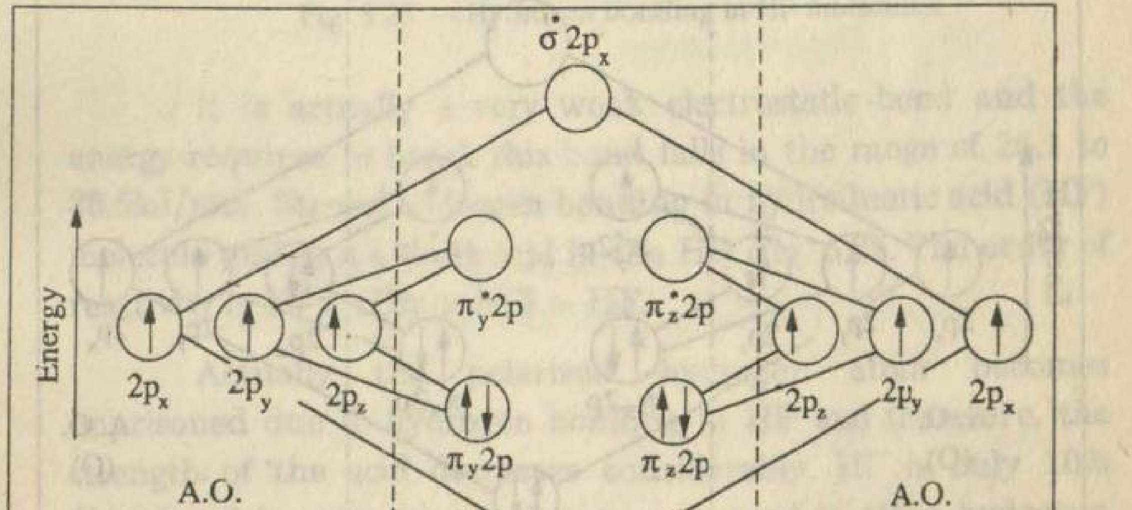


Fig. 5.23 — The formation of N_2 molecule.

remaining $(\sigma 2p_x)^2$ $(\pi\ 2p_y)^2$ and $(\pi\ 2p_z)^2$ orbitals give rise to a triple bond (bond order = 3) between two nitrogen atoms. The N≡N bond consists of a σ-bond and two π-bonds as shown in Fig (5.23).

$$2N \longrightarrow N_2$$

$$(1s^2, 2s^2, 2p^3) \qquad [kk(\sigma\ 2s)^2(\sigma^*2s)^2\ (\sigma\ 2p)^2\ (\pi 2p)^4]$$

5.14.1 Molecule of Oxygen and its Paramagnetic Nature

Each oxygen atom contributes six electrons to O_2 molecule from its valence shell. This means that 6 electrons must be placed into a set of the molecular orbitals. As shown in Fig. 5.23 two electrons enter into $2p_z$, two into each of the bonding π orbitals, π_{2p_x} and π_{2p_y}. The two electrons are placed in the $\pi^*_{2p_z}$ and $\pi^*_{2p_y}$ antibonding orbitals. However as both these electrons are of the same energy they spread themselves out with their spin in the same direction. The presence of these two unpaired epectrons impart paramagnetic property to O_2. Both VSEPR and VB fail to show unpaired electrons in O_2. The

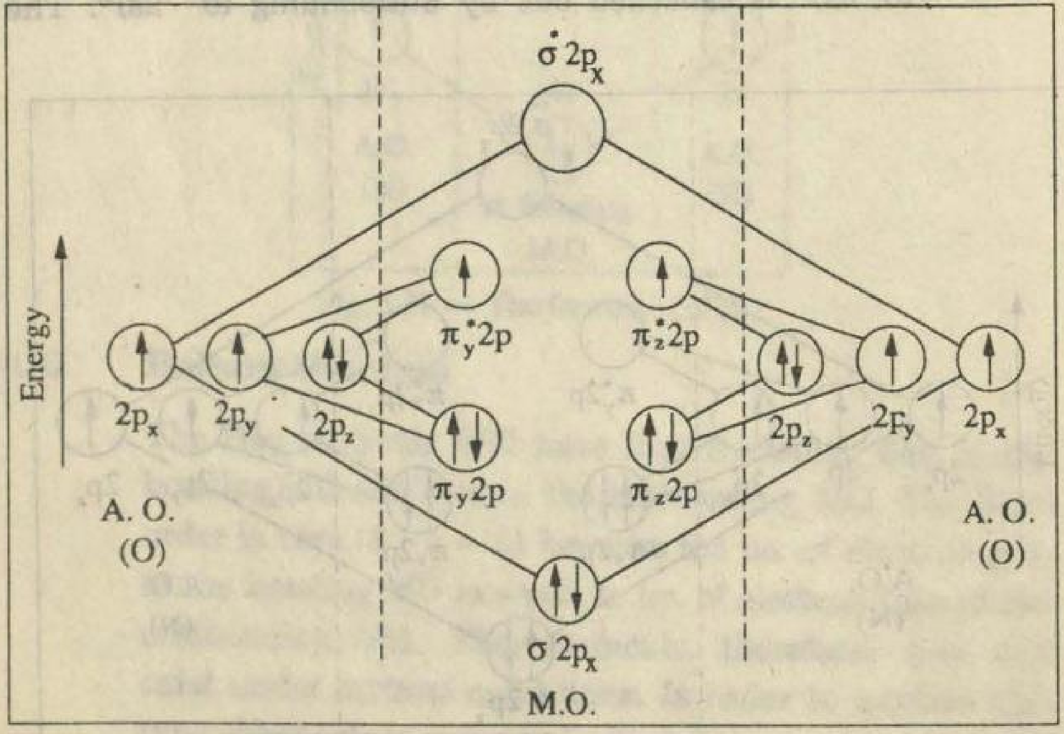


Fig. 5.24 — The formation of O_2 molecule.

molecular orbital theory successfully explains the presence of unpaired electrons in O_2 and in this respect it is superior to both the VSEPR and VB theories. The presence of unpaired electrons is indicated in Fig. 5.24

$$2O \longrightarrow O_2$$

$$(1s^2, 2s^2, 2p^4) \quad [kk(\sigma\ 2s)^2(\sigma^*2s)^2\ (\sigma\ 2p)^2\ (\pi 2p)^4(\pi^*2p_y)^1\ (\pi^*2p_z)^1]$$

5.15 Hydrogen Bonding

It is the attraction, largely electrostatic in nature, between the covalently bonded polarised hydrogen and a highly electronegative atoms like N, O and F. This bond is represented by a dotted line

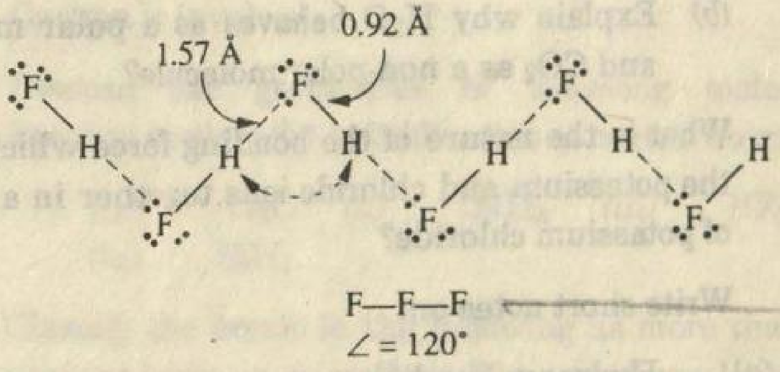


Fig. 5.25 — Hydrogen bonding in HF molecules.

It is actually a very weak electrostatic bond and the energy required to break this bond falls in the range of 25.1 to 33.5kJ/mol. Strong hydrogen bonding in hydrofluoric acid (HF) molecule makes it a weak acid in the HF, Fig. 5.25. The order of reactivity is HI > HBr > HCl > HF.

Actually the polarized hydrogen atom becomes imprisoned due to hydrogen bonding in HF and therefore, the strength of the acid decreases considerably. HF is only 10% dissociated in aqueous solution as compared to other hydrogen halides which are dissociated upto 92%.

The hydrogen bonding is of enormous importance in biochemical processes, specially the N—H....N bond, which

enables complex proteins and nucleic acids to be built up. This type of linkage is of great significance in life processes.

EXERCISE

1. **What is the difference between electrovalent bond, a covalent and a co-ordinate covalent bond?**

2. *(a)* **Explain why covalent bonds are stronger between unlike atoms?.**

   (b) **Explain why H_2O behaves as a polar molecule and CO_2 as a non-polar molecule?**

3. **What is the nature of the bonding force which holds the potassium and chloride ions together in a crystal of potassium chloride?**

4. **Write short notes on:**

   (a) **Hydrogen bonding.**

   (b) **Dipole moment.**

   (c) **Bond energy.**

   (d) **Shapes of common molecules.**

5. **Which of the following molecules will show dipole moment? Justify by drawing the geometries of molecules.**

(a)	Br—Br	*(g)*	SO_2
(b)	CH_4	*(h)*	C_6H_6
(c)	H—Cl	*(i)*	C_6H_5—CH_3
(d)	H_2O	*(j)*	CCl_4
(e)	Cl_2	*(k)*	C_2H_2
(f)	C_6H_5-Cl		

6. Differentiate between:

   (a) Sigma and Pi bond.

   (b) Polar and non-polar bond.

   (c) Atomic and molecular orbital.

   (d) Bonding and antibonding orbital.

7. What is orbital hybridization? Discuss different types of hybridization.

8. What is an atomic orbital? discuss the shapes of the sp^3 and sp^2 hybrid orbitals.

9. Discuss the orbital pictures of CH_4, C_2H_4 and C_2H_2 with reference to types of hybridization in which Carbon is involved.

10. Discuss the geometries of following molecules keeping in view the hybridization of central atom.

    (i) H_2O (ii) NH_3 (iii) BF_3
    (iv) SiH_4.

11. Classify the bonds in the following as more than 50 percent ionic or more than 50 percent covalent: Cl_2 HI, CaS, KBr, HCl, Cl_2O.

12. Select from the following list the molecules that contain one or more polar bonds; N_2, SO_3, H_2Se, Cl_2, ICl, SiH_4. should each of these molecules with polar bonds have a dipole moment. Explain.

13. Match the following compounds with its dipole moment.

Compound	Dipole moment
ClF	0.57 D
BrF	0.62 D
ICl	0.88 D
BrCl	1.29 D

14. Draw the orbital diagrams of the following molecules.

NH_3, H_2O, CCl_4, BF_3

15. Discuss how MO, Theory is superior to VB theory in some respect.

16. Fill in the blanks with suitable words given in the brackets.

(i) Energy is ________ when two atoms form a bond. (absorbed/released)

(ii) Ionic bonds is produced due to the transference of electron among the elements having ________ I.E. and ________ E.A. (high/low)

(iii) Water is a ________ molecule while CO_2 is ________ one .(nonpolar/polar)

(iv) ________ Compounds have relatively low M.P. and B.P. than ________ ones. (nonpolar/polar)

(v) Energy of bonding M.O. is ________ than atomic orbitals from which it is formed. (higher/lower)

(vi) The B.D.E. of H—Cl is ________ than the average values of H_2 and Cl_2. (less/greater)

(vii) The unit of dipole moment is ________ (Debye/poise)

(viii) Water has a ________ structure while CS_2 has ________ . (bent/linear)

(ix) Hybridized orbitals are ________ in energy than unhybridized ones. (lower/higher)

(x) The lone pair in NH_3 ________ the bond angle from tetrahedral value. (decreases/increases)

(xi) The bond angles of NH_3 and BF_3 are ________ (same/different)

(xiii) The hybridization of O and S in H_2O and H_2S is ________ (same/different)

(xiv) The hybridization of C in CH_4 is ________ in C_2H_4 is ________ and in C_2H_2 is ________ $(sp/sp^2/sp^3)$

(xv) The structure of C_2H_2 ________ but that of C_2H_4 is ________. non linear/linear)

(xvi) The reaction of ionic compounds are usually very ________ (fast/slow)

(xvii) O_2 is ________ while N_2 is ________ (Para magnetic/dia-magnetic)

(xviii) HF is an exceptionally weaker acid due to ________ (vander Waal's forces/H bonding

(xix) Molecular orbital theory is ________ to valence bond theory. (not superior/superior)

(xx) π-bond is ________ than a σ - bond for two same atoms. (stable/unstable)

(xxi) A bond formed due to electron transference is called ________ (Ionic/Covalent)

(xxii) The ________ bonds are always non-directional. (Ionic/Cov)

(xxiii) The sigma bond is ________ than Pi bond. (stronger/weaker)

(xxiv) The sp^3 orbitals are ________ (coplanar/non-coplanar)

17. Explain the following with reasons:

(a) NaCl is a harder substance at room temperature than glucose.

(b) No bond in chemistry is 100% ionic.

(c) A double bond is shorter and stronger than a single bond.

(d) NH_3 and H_2O can form Co-ordinate covalent bond with H^+ but CH_4 cannot do so.

(e) Covalent bond may be non-polar but co-ordinate covalent bond is always polar.

(f) The dipole moments of NH_3 and PH_3 are 1.47 D and 0.56 respectively but are zero for BF_3 and SO_3 although all the four molecules are tetra-atomic.

(g) BF_3, BCl_3, $AlCl_3$, are triangular planar molecules, but NH_3, NF_3 and PCl_3 etc. are triangular pyramids although in all these compounds, the central atom is connected with three other atoms.

(h) Oxygen, nitrogen and carbon atoms are SP^3 hybridized in H_2O, NH_3 and CH_4, but the bond angles are not equal.

(i) π-bond is only formed between two atoms, when a sigma bond is already there.

(j) Molecule of O_2 is paramagnetic in nature.

6

ENERGETICS OF CHEMICAL REACTIONS

6.1 Introduction

The idea of energy is basic to our way of living. We use this term frequently in all sorts of contexts ranging from energy required in playing games to energy crisis in the world.

The SI unit of heat and energy is the joule (J). One joule is the energy spent when a force of one newton acts over a distance of one metre. However, since the heat changes associated with chemical reactions are usually large, it is preferable to express them in kilojoules (1000 J) abbreviated as kJ.

Some other units and their joule equivalence is as under:

Name	Symbol	Joule Equivalence
Calorie	cal.	4.184J
Kilocalorie	k cal	4.184×10^3J
British Thermal Unit	B.T.U.	1.055×10^3J
Kilowatt Hours	kWh	3.6×10^3J

6.2 Why Does a Chemical Reaction Occur?

It is the natural tendency of any system when left to itself to attain the position of lowest energy state. This is observed in all branches of science and is the basis of second law of thermodynamics.

There are many common examples of this tendency. Water flows from higher levels to lower levels, heat flows from hotter body to colder ones, and electrical charge flows from higher potential to lower potential. So it is not surprising that all chemical reactions which proceed spontaneously, are accompanied by loss of energy in the system. In most of the cases, there is a net evolution of heat i.e., the reaction is exothermic overall.

Now, we have to think that why all such reactions do not proceed vigorously and with appreciable speed. For example, why a lump of coal does not burst into flames when exposed to air, although its combustion is a highly exothermic reaction. Similarly why a mixture of H_2 and O_2 remains unchanged after mixing, although the chemical reaction between oxygen and hydrogen to form water is a highly exothermic reaction.

6.2.1 Heat Changes in Chemical Reactions

Energy changes accompanying chemical reactions, under certain conditions, also appear in the form of light, electricity and mechanical work. These can be put to a number of useful purposes. Thus, the heat evolved in the burning of carbon in oxygen producing carbon dioxide is responsible for the

use of charcoal, coal or coke as a fuel. Natural gas acts as a fuel due to the combustion of methane in air evolving a large amount of heat. The heat evolved in the burning of acetylene in oxygen in an oxyacetylene flame is used for welding purposes. A part of the heat is converted into light as well.

The ignition of a mixture of petrol and air in a motor engine evolves a large amount of heat, a part of which is converted into mechanical work for driving the automobile.

Similarly in galvanic cells, a part of the heat of reaction is used in generating electric current.

The branch of chemistry which deals with thermal energy changes in chemical reactions is called thermochemistry. Since different substances have different amounts of energy, the total energy of the products of a chemical reaction may be different from the total energy of the reactants. So it is evident that the process may be accompanied by an absorption or evolution of energy in the form of heat. If heat is evolved in the reaction, the process is said to be exothermic, but if heat is absorbed it is described as an endothermic process. The majority of chemical reactions which go to virtual completion at ordinary temperature are exothermic.

The amount of heat evolved or absorbed in a chemical reaction, when the molar quantities of the products and the reactants being the same as represented in the chemical equation, is called heat of reaction. The heat of reaction is included in the equation with a positive sign if it is evolved and with a negative sign if absorbed from the surroundings. The physical state of each reactant and each product is also mentioned in these equations. A few examples of such equations for the reactions taking place at constant pressure and at 25°C are given below:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.51kJ$

(ii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(\ell)}$ $\Delta H = -571.66kJ$

(iii) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H = -890.4kJ$

(iv) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ $\Delta H = -92.33kJ$

(v) $4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s}$ $\Delta H = -1648.4kJ$

(vi) $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$ $\Delta H = -296.83kJ$

(vii) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$ $\Delta H = +52.96kJ$

(viii) $C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$ $\Delta H = 131.4kJ$

The first equation means that when 1 mole (12 g) of solid carbon reacts with 1 mole (32 g) of gaseous oxygen to give 1 mole (44 g) of carbon dioxide gas at 25°C and at constant pressure, 393.51kJ of heat is evolved.

The second equation implies that when 2 moles (4.032 g) of hydrogen combine with 1 mole (32 g) of oxygen, to give 2 moles (36.032 g) of water in liquid state at 25°C and at atmospheric pressure, the heat evolved is 571.66kJ. Both of these reactions are exothermic.

The equation (viii) shows that when 1 mole of steam (18.016 g) reacts with 1 mole of carbon (12 g) producing 1 mole (28 g) of carbon monoxide gas and 1 mole (2.016 g) of hydrogen gas, the heat absorbed is 131.4kJ. This is an endothermic reaction.

Similarly the equation *(iii)* to (vii) can be explained as equations *(i)*, *(ii)* and (viii).

6.2.2 System and Surroundings

The branch of science which deals with energy transformations is known as thermodynamics. In the study of thermodynamics it is always convenient to identify the system and its surroundings. A chemical system is usually the substance undergoing a physical or chemical change. The surrounding is everything in the universe that is not part of the system. For example, in the study of thermal decomposition of lead nitrate $Pb(NO_3)_2$, the sample of compound, would be defined as the system, whereas, the beaker, the source of heat and .everything else would be the surroundings. Most of the

changes in chemical systems are accompanied by heat changes. A process which releases heat from the system to the surroundings is referred to as exothermic. Thus the reaction of calcium oxide (CaO) with water which releases lot of heat to the surroundings is an exothermic process whereas; the thermal decomposition of lead nitrate in which heat is transferred from the surroundings to the system is an endothermic process.

6.3 Internal Energy of a Chemical System

The total energy contained within a chemical system is referred to as its internal energy, E. Internal energy is the sum of all the energies of all the atoms, molecules or ions within a system. It depends on the motion of molecules, i.e., translational, vibrational, rotational, their intermolecular and intramolecular forces. In other words, it is the total energy possessed by the system as a consequence of the kinetic energy of its atoms, ions or molecules, plus the potential energy that arises from the binding forces between the particles that make up the system. The internal energy E, of a system cannot be determined. However, change in internal energy denoted by ΔE can both be measured and calculated.

The state of a system is described in terms of temperature, pressure and volume.

Any property, that depends on the state of a system is called state function i.e. enthalpy, free energy and entropy.

The properties of the substance are, uniquely determined by the thermodynamic state of the system. A thermodynamic state is macroscopic condition of a system for which its properties are uniquely determined and are independent of time. Volume, temperature and pressure are also examples of state functions.

Change in a state function depends only on the initial and final states and not on the path through which the change is brought about.

Internal energy E of a system is also a state function and depends only on the initial and final states of the system.

$$\text{Thus} \quad \Delta E = E_{final} - E_{initial}$$

The internal energy change ΔE of a system is the amount of energy exchanged with the surroundings during a chemical or physical change of system.

An increase in the internal energy of a chemical system has three possible results:

(i) Increase in internal energy of a system can increase the temperature of the system by increasing the kinetic energy of the molecules.

(ii) Increase in internal energy of a system can result in phase change of a system. For example, melting or vaporization can occur.

(iii) Increase in internal energy can result in a chemical reaction. When increase in internal energy is sufficient to break the bonds, a chemical reaction can take place.

A decrease in internal energy appears usually as a decrease in thermal energy of the system but can rarely initiate a chemical reaction.

6.3.1 Internal Energy and Law of Conservation of Energy

Let the initial state of a system be represented by A and the final state by B (Fig. 6.1) and let E_A and E_B represent energy associated with the system in its states A and B respectively. The change in the system from state A to state B will involve change in energy of the system and is given by

$$\Delta E = E_B - E_A.$$

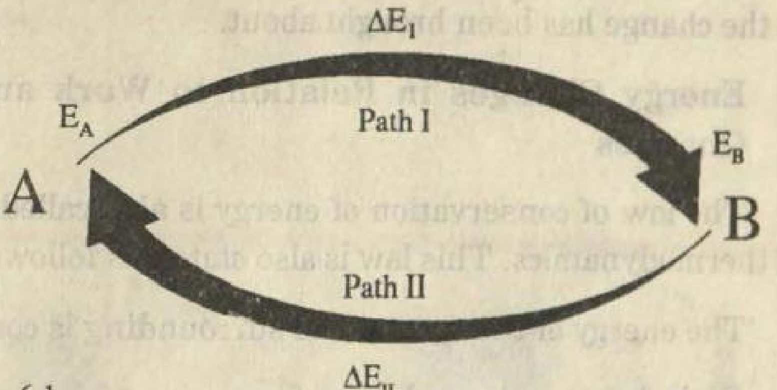


Fig. 6.1

ΔE is a definite quantity, irrespective of the path or manner in which the change has been brought about. If it were not so, it would be possible to construct a machine which can produce energy without expenditure of energy, which is contrary to the law of conservation of energy. The law of conservation of energy states that energy can neither be created nor destroyed, although it can be transformed from one form to another. Thus, whenever energy in one form disappears, an equal amount of energy in some other form must appear.

Suppose, for example, the system changes from state A to state B by following the path I and is accompanied by increase of energy equal to ΔE_1. Now suppose that the same change of state is brought about by another path II, and the increase of energy, is ΔE_2. If ΔE_1 is not equal to ΔE_2 e.g. $\Delta E_1 > \Delta E_2$. Then, by a coupling of these two processes.

$$A \longrightarrow B \text{(by path-I)}$$

and

$$B \longrightarrow A \text{(by path-II)}$$

the system would return to its initial state and at the same time a surplus of energy equal to $\Delta E_1 - \Delta E_2$ would become available. By repeating the same cycle over and over again, energy would be produced continuously. This is contrary to law of conservation of energy (first law of thermodynamics). Hence $\Delta E_1 = \Delta E_2$. Thus, the energy change accompanying a process is a state function which depends only on the initial and final states

of the system and is independent of the path or the manner by which the change has been brought about.

6.4 Energy Changes in Relation to Work and Heat Changes

The law of conservation of energy is also called the first law of thermodynamics. This law is also stated as follows:

"The energy of the system and surrounding is conserved".

Both heat and work are forms in which energy is transferred into and out of a system. In many processes both heat and work cross the boundary of the system and the energy change is the sum of both heat and work so that total energy of the system and its surroundings remains constant. Thus in an interaction between a system and its surroundings, the entire energy change ΔE must be accounted for by heat q and work w.

$$\Delta E = q + w \text{ .... } (i)$$

This is the mathematical form of the first law of thermodynamics.

In this form of the law, ΔE is negative when a system loses energy and is positive when a system gains energy. When heat has been added to the system and work has been done on a system, both of which increase the internal energy of the system, q and w are given positive values. Heat lost by a system or work done by a system on the surroundings—both of which can decrease the internal energy of the system—are given negative values.

Work is done when a system expands against an opposing pressure. Work is always accomplished when an opposing force is pushed through a distance. Mathematically,

Work = force x distance

Let us consider a gas enclosed in a cylinder fitted with a position as shown in Fig 6.2. An external pressure P exerted by a

force F spreads over the area A of a piston. As pressure is force per unit area,

$$P = \frac{F}{A}, \text{ therefore}, F = P \times A$$

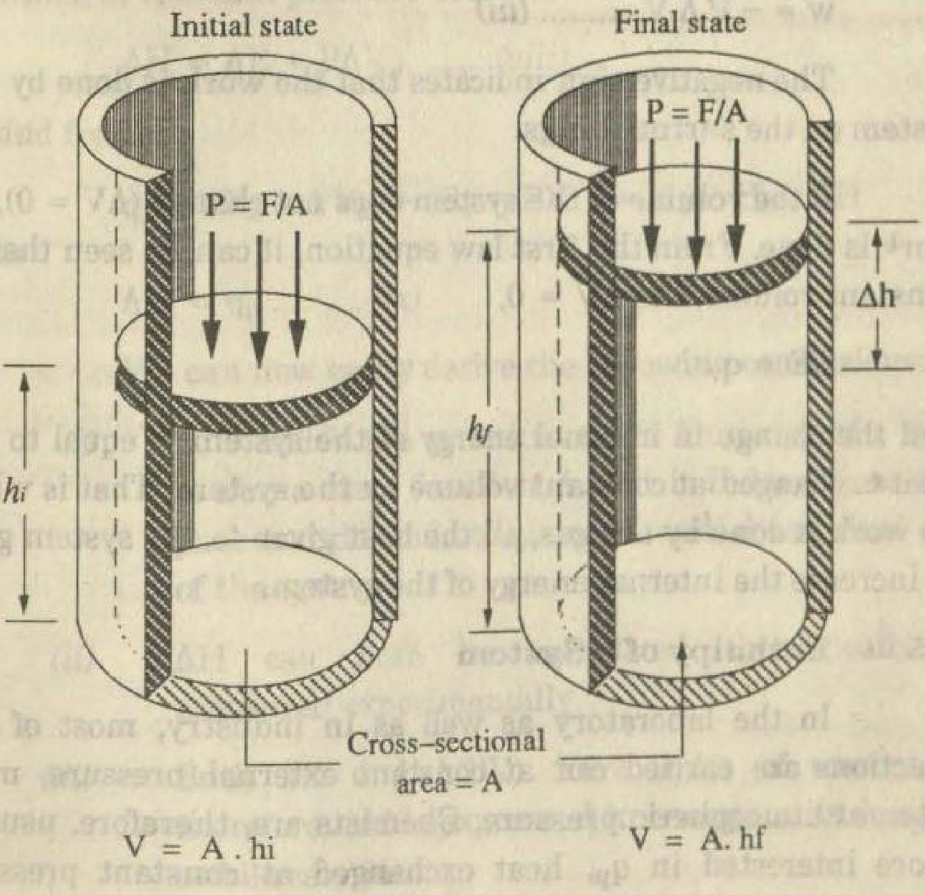


Fig. 6.2 — Pressure volume work

Volume of the gas in the cylinder is equal to the cross-sectional area A, multiplied by the height of column of gas, h

$$V = A \times h$$

Now let us assume that the gas expands and does work by pushing the piston against external pressure. 'A' remains the same but 'h' changes. The volume change is therefore,

$$\Delta V = V_f - V_i$$

$$\Delta V = Ah_f - Ah_i$$

$$\Delta V = A(h_f - h_i)$$

$\Delta V = A\Delta h$ .... *(ii)*

Work done by the expanding gas against a constant external pressure is given by:

$w = -F \times A \times \Delta h$

$w = -P\,\Delta V$ .... *(iii)*

The negative sign indicates that the work is done by the system on the surroundings.

If the volume of the system does not change ($\Delta V = 0$), no work is done. From the first law equation, it can be seen that at constant volume, i.e., $\Delta V = 0$,

$\Delta E = q_v$

and the change in internal energy of the system is equal to the heat exchanged at constant volume by the system. That is when no work is done by the gas, all the heat given to the system goes to increase the internal energy of the system.

6.5 Enthalpy of a System

In the laboratory as well as in industry, most of the reactions are carried out at constant external pressure, most often at atmospheric pressure. Chemists are, therefore, usually more interested in q_p, heat exchanged at constant pressure rather than q_v. For a system at constant pressure, which can exchange energy with the surroundings only as heat or work, the equation for the first law of thermodynamics can be written as:

$\Delta E = q_p + w$

Putting the value of w from equation *(iii)*

$\Delta E = q_p - P\Delta V$ .... *(iv)*

or $E_2 - E_1 = q_p - P(V_2 - V_1)$

$E_2 - E_1 = q_p - PV_2 + PV_1$

rearranging gives

$q_p = (E_2 + PV_2) - (E_1 + PV_1)$ .... *(v)*

Now we define enthalpy H as

$$H = E + PV \text{ .... } (vi)$$

so that

$$\Delta H = \Delta E + \Delta(PV) \text{ .... } (vii)$$

which at constant pressure becomes

$$\Delta H = \Delta E + P\Delta V \text{ .... } (viii)$$

and from *(v)*

$$q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$$

or

$$\Delta H = q_p \text{ .... } (ix)$$

We can now easily derive the following conclusions:

(i) E, P and V are state functions. Enthalpy of a system is also a state function, i.e., it is independent of the path and depends only on the initial and final states of the system.

(ii) ΔH can both be calculated theoretically and measured experimentally.

(iii) Both ΔE and $\Delta(PV)$ have units of energy, and therefore, ΔH is expressed in energy units, kilojoules or kilo calories.

(iv) Many processes involving solids and liquids, the value of ΔV being very small, the term $\Delta(PV)$ can be neglected and $\Delta H = \Delta E$.

(v) If a reaction takes place at constant temperature, usually room temperature (298K) and constant pressure, ΔH gives a measure of the heat of reaction, the quantities of products and reactants being the same as represented by the chemical equations.

6.5.1 Standard Enthalpy Changes

Enthalpy changes in chemical reactions are usually expressed for reactants and products in their standard states.

The symbol for 'standard enthalpy change' is ΔH^o. The temperature at which standard enthalpy changes are measured is 298 K (room temperature). For this reason standard enthalpy change of process, chemical or physical, is also represented by the symbol ΔH^o_{298}. Similarly when internal energy changes for substances in their states are to be expressed, the symbol used is ΔE^o. Those reactions which do not actually take place at room temperature and require higher or lower temperatures, the standard enthalpy changes at 298K are calculated from ΔH values measured at other temperatures.

6.5.2 Standard Heat of Formation

The standard heat of formation of a compound is the enthalpy change accompanying the formation of one mole of a compound, all substances being in their standard states. It is denoted by ΔH_f^o. The standard state of any substance is taken as its natural state at 298K (25°C) under one atmospheric pressure.

The heats of formation of the compounds involved in a reaction have an important connection with the heat of reaction. For purposes of calculations the heat contents of all elements in their standard states are arbitrarily taken to be zero. The heat of formation of a compound is then equal to the heat of reaction ΔH involving formation of one mole of the compound from elements in their standard states i.e., at 25°C and at one atmospheric pressure. This may be illustrated by the following example.

Consider the reaction between carbon and oxygen at 25°C to give carbon dioxide under one atmospheric pressure.

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta H - 393.51 kJ/mol$$

Thus, standard heat of formation of carbon dioxide,

$$\Delta H^o_f = -393.51 \text{ kJ/mole by definition.}$$

Similarly, the reaction between sulphur and oxygen at 25°C to give sulphur dioxide at one atmospheric pressure is,

$$S(s) + O_2(g) \longrightarrow SO_2(g)\ \Delta H^o_f = -296.83 kJ$$

This means, that standard heat of formation of sulphur dioxides, is $\Delta H^o = -296.6kJ$ by definition.

Standard heats of formation or standard enthalpies of formation of a few substances are given in Table 6.1 below. These values of ΔH^o_f are for the formation of one mole of given substance in their standard states at 298K. Solids which have more than one crystalline forms possess different ΔH^o_f values.

Table 6.1
Standard Enthalpies of Formation at 298k

Substance	ΔH^o_f (kJ/mole)	Substance	ΔH^o_f (kJ/mole)
Standard state	0.00	$CaC_{2(s)}$	– 62.5
of all elements		$CS_{2(\ell)}$	89.70
C(graphite)	0.00	$HCl_{(g)}$	– 92.31
C(diamond)	1.90	$NaCl_{(s)}$	– 411.00
$P_{(s)}$ (white)	0.00	$HBr_{(g)}$	– 36.40
$P_{(s)}$ (red)	– 17.60	$HI_{(g)}$	26.48
$H_2O_{(\ell)}$	– 285.83	$NH_{3(g)}$	– 46.11
$SO_{2(g)}$	– 296.83	$H_2S_{(g)}$	– 20.63
$CO_{(g)}$	– 110.53	$CH_{4(g)}$	– 74.81
$CO_{2(g)}$	– 393.51	$C_2H_{2(g)}$	226.73
$Fe_2O_{3(s)}$	– 824.2	$H_2SO_{4(l)}$	– 813.99
$Fe_3O_{4(s)}$	– 1118.4	$HNO_{3(l)}$	– 174.10
$CaO_{(s)}$	– 635.5	$Ca(OH)_{2(aq)}$	– 1002.82

6.6 Hess's law of Constant Heat Summation

The calculations of heats of reaction and heat of formation given above have been based on the principle of conservation of energy and hence on the first law of thermodynamics. Two important thermochemical laws are based on the same principle. The first one states that "quantity of heat required to decompose a compound into its elements is equal to the heat evolved when that compound is formed from

its elements; that is, the heat of decomposition of a compound is equal to its heat of formation, but with opposite sign.

The second important law of thermochemistry was discovered experimentally by G.H. Hess in 1840. It states that the amount of heat evolved or absorbed in a process, including a chemical change, is the same whether the process takes place in one or several steps. This means that the net heat of reaction depends only on the initial and final states, and not on the intermediate states through which the system may pass. The Hess's law, often called the law of constant heat summation, is a direct consequence of the law of conservation of energy.

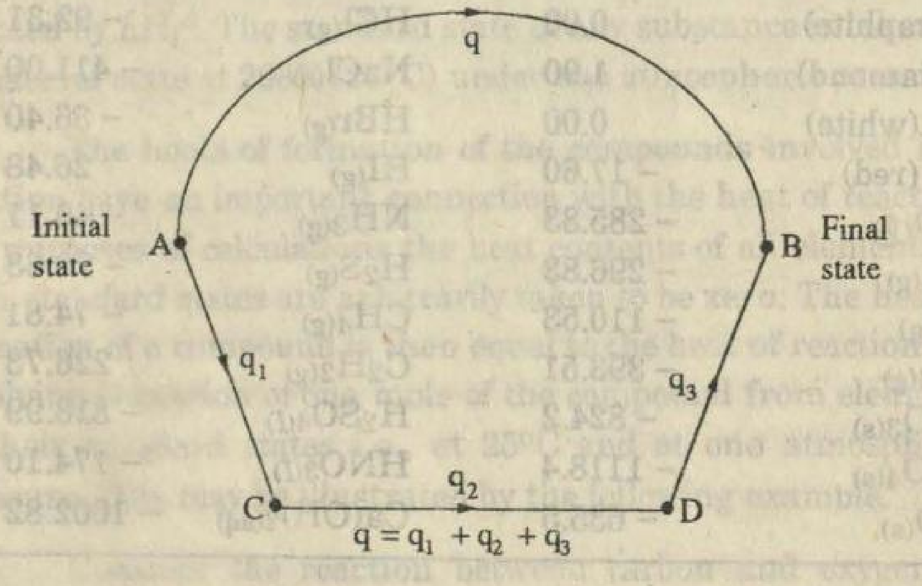


Fig. 6.3

Suppose in a process, the system changes from state A to state B in one step and heat evolved in this change is q. Now suppose the system changes from state A to state B in three steps involving a change from A to C, C to D and finally from D to B, as shown in Fig. 6.3. If q_1, q_2 and q_3 are the heats evolved in the first, second and third step respectively, then, according to Hess's law $q_1 + q_2 + q_3 = q$

6.6.1 Applications of Hess's law

(i) Heat of Formation

The law may be illustrated by considering the formation of an aqueous solution of ammonium chloride from ammonia, hydrogen chloride and water. There are two ways in which this reaction can be brought about.

First way

$$NH_3(g) + HCl(g) + aq \longrightarrow NH_4Cl(aq)\ \Delta H = -159.89kJ$$

Second way

$$NH_3(g) + aq \longrightarrow NH_3(aq) \quad \Delta H_1 = -35.16kJ\ (i)$$

$$HCl(g) + aq \longrightarrow HCl(aq) \quad \Delta H_2 = -72.41kJ\ (ii)$$

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)\ \Delta H_3 = -51.48kJ\ (iii)$$

Summing up (i), *(ii)* and *(iii)*

$$NH_3(g) + HCl(g) + aq \longrightarrow NH_4Cl(aq)\ \Delta H = -159.05kJ$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -159.05kJ$$

It is seen that the heat change in either case is almost the same.

(ii) Heat of Combustion

Similarly, the combustion of carbon to carbon dioxide, CO_2, evolves 393.51kJ of energy. On the other hand, when reaction forms carbon monoxide i.e., by burning of carbon in limited supply of air, the value of ΔH is −110.53kJ. Burning CO to produce CO_2 release 282.98kJ of energy. The sum of the two reactions $C \longrightarrow CO$ and $CO \longrightarrow CO_2$ give the overall reactions.

First way

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta H = -393.51kJ$$

Second way

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \quad \Delta H_1 = -110.53kJ$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2 \quad \Delta H_2 = -282.98kJ$$

By adding

$$C(s) + O_2(g) \longrightarrow CO_2(g) \; \Delta H = -393.51kJ$$

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$= -393.51kJ$$

The sum of the two enthalpy changes is ΔH for the overall reaction. The above case illustrates the fact that we can treat thermochemical equations algebraically.

(iii) Indirect Measurement of ΔH

Hess's Law is particularly useful in situations in which direct measurement of an enthalpy change is not feasible. Some reactions occur too slowly to permit us to measure the enthalpy changes directly in a precise manner and some do not take place cleanly; that is, they do not produce a single product or a single set of products. For instance, the combustion of carbon to carbon monoxide forms some carbon dioxide at the same time. Therefore, two separate measurements in the calorimeter for the reactions $C \longrightarrow CO$ and $CO \longrightarrow CO_2$ are made. From the values of ΔH for these reactions. ΔH for the reaction $C \longrightarrow CO$ is found by difference.

An example of a reaction which takes place so slowly that we cannot measure the enthalpy change is the formation of methane from carbon and hydrogen.

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \text{......... (i)}$$

However each of the three substances in this equation undergoes combustion. The three combustion reactions and the enthalpy changes are:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O \; \Delta H = -890.4kJ \quad \textit{(ii)}$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell) \quad \Delta H = -285.8kJ \quad \textit{(iii)}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.7kJ \quad \textit{(iv)}$$

To calculate ΔH for the equation *(i)*, adjust eqs. *(ii)* and *(iii)* so that each substance in eq. *(i)* appears on the proper side. Multiply eq. *(iii)* by 2, so that $2H_2$ will be on left and then add the three equations:

$$2H_2O(\ell) + CO_2(g) \longrightarrow CH_4(g) + 2O_2(g) \quad \Delta H = +890.4kJ$$

$$2H_2(\ell) + O_2(g) \longrightarrow 2H_2O(\ell) \quad \Delta H = -571.6kJ$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.7kJ$$

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta H = -74.9kJ$$

The result is the equation for the reaction *(i)* and its ΔH which we can not measure directly.

EXERCISE

1. Explain the term: heat of reaction. Explain why is it essential to mention the physical states of reactants and products in a thermochemical equation.

2. Discuss carefully the change of internal energy and the change of enthalpy taking place in chemical reactions.

3. What is meant by heat of reaction? Explain how the heat of reaction at constant volume differs from the heat of reaction at constant pressure.

4. Explain the term standard enthalpy of formation.

5. State and explain Hess's law. Show clearly that this law is only a special case of the first law of thermodynamics.

6. State and discuss the laws of thermo-chemistry.

7. Calculate the ΔH for the sublimation of one mole of iodine from the following data.

(i) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ $\Delta H = 51.8 kJ/mol$

(ii) $H_2(g) + I_2(l) \longrightarrow 2HI(g)$ $\Delta H = -10.5 kJ/mol$

8. Calculate the heat of formation of ethyne, C_2H_2 from the following data.

(i) $C + O_2 \longrightarrow CO_2 + -393.7 kJ$

(ii) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O + 284.3 kJ$

(iii) $C_2H_2 + 5O_2 \longrightarrow 2CO_2 + H_2O + 1296 kJ$

9. Liquid ethanol when burnt in oxygen at 25°C shows $\Delta H = -1402.14 kJ$. Heats of formation of $CO_2(g)$ and $H_2O(\ell)$ are − 393.51kJ and − 285.83kJ, respectively at the same temperature. Calculate the heat of formation of ethanol at 25°C.

Ans: $\Delta H = -243$ kJ/mol.

10. Calculate the enthalpy change for the reaction. From the enthalpy changes for the combustion of Al and Fe.

$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$

(i) $2Al(s) + {}^3/_2\, O_2(g) \longrightarrow Al_2O_3(s)$ $\Delta H = -1675.7 kJ$

(ii) $2Fe(s) + {}^3/_2\, O_2(g) \longrightarrow Fe_2O_3(s)$ $\Delta H = 824.2 kJ$

Ans: $\Delta H = -845.5 kJ$

11. Fill in the blanks with suitable words given in the brackets.

(i) Systems always move from __________ energy state to __________ energy state. (lower/higher)

(ii) Negative enthalpy change of a chemical reaction __________ that reaction is spontaneous. (means/does not mean)

(iii) __________ is a state function. (enthalpy/ enthalpy change)

(iv) Internal energy/always equal to enthalpy change of a chemical reaction (is/is not).

(v) First law of thermodynamics is ____________ law of conservation of energy. (is/is not)

(vi) Pressure-volume work is ____________ . ($P\Delta V$/ $V\Delta P$)

(vii) Heat supplied to a gaseous system at constant pressure is ____________ than heat supplied at constant volume. (less/greater)

(viii) Standard en :haply of formation of a substance is ____________ negative. (always/not always)

(ix) When the work is done on the system by the surrounding, the sign of work done is ____________ . (+ Ve/ -Ve)

(x) Heat of formation of liquid water is ____________ than heat of formation of gaseous water. (less/more)

(xi) 1 calorie = ____________ kJ. (4.184/41.84 /0.004184)

(xii) Standard enthalpies are measured at ____________. (273K/298K/373K)

12. Explain the following with reasons:-

(a) Exothermic reactions aı e mostly spontaneous.

(b) It is essential to mentio: the physical states of reactants and products 'n a thermochemical equation.

(c) Heat is evolved when stron,'er bonds are being formed and is absorbed wher. weaker bonds are formed.

(d) The process at constant pı essure involves pressure volume work.

(e) Hess's law is employed to calcula:e ΔH value of a chemical reaction indirectly.

7

CHEMICAL EQUILIBRIUM

7.1 Introduction

When a sample of liquid water is placed in closed container at constant temperature, part of the liquid vaporizes. As water begins to vaporize, the vapours also begin to condense, although the rate of vaporization is more than the rate of condensation. As time passes the concentration of molecules in the vapour state increases, so does the rate of condensation, eventually it becomes equal to the rate of vaporization Fig.(3.3). When this happens we may say that the liquid and vapours are in a state of dynamic equilibrium.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

The double arrow implies that at the equilibrium state the forward process and reverse process are occurring at the same rate. As a result of dynamic equilibrium, concentration of

water vapours becomes constant and does not change with time, so long as the temperature remains constant.

Chemical reactions carried out in closed containers show some resemblance to phase changes as described above. It is well established that many reactions do not go to completion. They proceed to a certain extent and then apparently stop. The reactants are not completely consumed. Instead we obtain an equilibrium mixture containing both reactants and products. Under any given set of conditions of temperature, pressure and concentration, the point at which any reaction seems to stop is always the same *i.e.* there exists a quantitative relationship among the concentrations of various reactants and products which is definitely fixed. When a reaction reaches this stage, it is said to have attained equilibrium.

7.2 The Equilibrium State

A state of a chemical equilibrium should not be considered the state of a reaction at which all motions cease of. It is much more fruitful to consider the point of equilibrium as the state in which the rate at which the reactants disappear to form the products is exactly equal to the rate at which the products interact to reproduce the reacting substances. The change of concentration of reactants or products is called rate of reaction. Under these conditions no perceptible transformation can be detected in the system, and the net effect is an apparent state of complete rest. Such an equilibrium is designated as a dynamic one, in contrast to a static equilibrium where there is no motion what so ever. All chemical equilibria and equilibria between physical states are considered to be dynamic in nature.

Let us consider what happens when a sample of nitrogen tetraoxide N_2O_4, a colourless gas is placed in a closed evacuated container and heated to 100°C. Instantaneously a reddish brown colour develops. This colour is due to nitrogen dioxide, NO_2 formed by the decomposition of a part of the N_2O_4.

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)} \quad \text{..............} \quad (A)$$

At first this is the only reaction taking place. However, as soon as some NO_2 is formed the reverse reaction occurs.

$$2NO_{2(g)} \longrightarrow N_2O_{4(g)} \quad .... \quad (B)$$

As time passes, reaction (A) slows down and (B) speeds up. Soon the rates become equal. A dynamic equilibrium is established.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

At equilibrium, appreciable amounts of both gases are present. From that point on, their concentrations remain constant, so long as the volume of the container and the temperature remain unchanged.

The approach to equilibrium in this system is illustrated by the Fig. 7.1. We start with 0.1M N_2O_4 in a container at 100°C. The original concentration of N_2O_4 is thus 0.100 mol/dm^3. Since there is no NO_2 present at the beginning of the experiment, its initial concentration is zero.

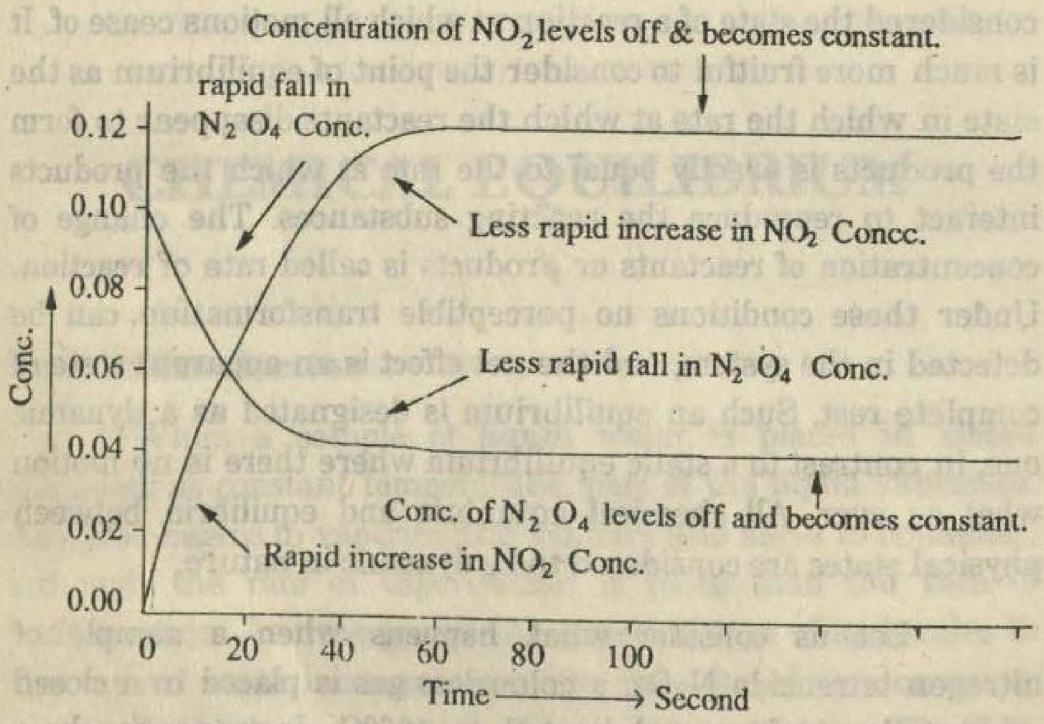


Fig. 7.1

As the equilibrium is approached the net reaction taking place is that in the forward direction. The concentration of N_2O_4

drops and that of NO_2 increases. Finally, both concentrations level off and become constant. This tells us that the reaction has attained the equilibrium. Notice that at any time during the reaction the increase in concentration of NO_2 is exactly twice the decrease in concentration of N_2O_4.

Consider, for example what happens in the 60 seconds required to reach equilibrium. The concentration of N_2O_4 decreases by 0.06 mol/dm^3.

Initial concentration of N_2O_4 = 0.10 M

Decrease in concentration of N_2O_4 = 0.060 M

Concentration of N_2O_4 at equilibrium = 0.10–0.06 M

= 0.04 M

Now concentration of NO_2 must be equal to twice the decrease in concentration of N_2O_4.

Therefore concentration of NO_2 at equilibrium = 0.06x2 = 0.12M

The relationship is explained quite simply, as given by the following equation.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

From the co-efficients of the balanced equation we see that two moles of NO_2 are formed for every mole of N_2O_4 that decomposes. Hence if 'x' moles of N_2O_4 decompose, 2x moles of NO_2 form. If the concentration of N_2O_4 decreases by x mole/dm^3 that of NO_2 must increase by twice that amount, i.e., 2x moles/dm^3.

As a result of the above observations the following deductions or conclusions are the natural outcome i.e.

(*i*) Reversibility and chemical equilibrium are related with each other.

(*ii*) There is a rapid fall or increase in the concentrations of the reactants and products in the beginning and less rapid later on. This suggests that there must be

some relationship between the concentrations of the active masses of the reacting species and the rate of reaction. This led Guldberg and Waage in 1869 to put forth a law, known as law of mass action.

7.3 The Law of Mass Action

This law states, "*The rate at which a substance reacts, is directly proportional to its active mass and the rate of a reaction is directly proportional to the product of the active masses of the reacting substances*".

For example, consider a general reaction *i.e.*.

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

The active masses, in terms of molar concentration of A, B, C and D are represented by [A], [B], [C], and [D] respectively.

According to the law of mass action:

The rate of forward reaction is proportional to [A] [B] and therefore the rate of forward reaction is equal to k_f [A] [B], while the rate of reverse reaction = k_r [C] [D] where k_f and k_r are the *rate constants for* the forward and reverse reactions, respectively.

At the equilibrium state:

$$\text{Forward rate} = \text{Reverse rate}$$

$$k_f [A] [B] = k_r [C] [D]$$

$$\frac{[C] [D]}{[A] [B]} = \frac{k_f}{k_r} = K_c \quad \text{.............} \quad 7.1$$

Where K_c is called the equilibrium constant. The subscript 'c' indicates the concentration of various species at the equilibrium point in terms of moles per litre. Notice that in the expression for K_c the equilibrium concentrations of the products

(right side of equation) appear in the numerator, that of the reactants (left side of equations) as denominators. The value of K_c is independent of the initial concentrations of the reactants at a given temperature. However it varies with temperature and remains constant at a constant temperature. The equilibrium constant K_c has no units.

For gaseous equilibria, the concentrations are measured in terms of their partial pressures and equilibrium constant is expressed as K_p.

For a more general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium expression is given by

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad \text{.........................} \qquad (7.2)$$

Where, a, b, c, and d in equation (7.2) are the coefficients in the balanced equation of A, B, C, and D. The coefficients appear as the exponents of the concentration terms in the equilibrium constant expression.

The concentrations of gaseous substances are expressed in terms of their partial pressures.

$$Kp = \frac{\text{Product of partial pressure of gaseous products}}{\text{Product of partial pressure of gaseous reactants}}$$

Where Kp is the equilibrium constant when the concentrations are expressed in terms of partial pressures.

To illustrate the application of this law, consider the system

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

For these reactions the equilibrium constants can be expressed as

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Since the substances involed are gaseous in nature so their expression of K_p are:

$$K_p = \frac{P_{H_2} P_{I_2}}{P_{2HI}}$$

$$K_p = \frac{P_{2_{NH_3}}}{P_{3H_2} P_{N_2}}$$

Where P_{H_2} P_{I_2} etc represent the partial pressures of gaseous solution at equilibrium state.

Example 1

An equilibrium mixture of N_2, H_2 and NH_3 at 300°C is analysed, and it is found that; $[N_2]$ = 0.25M, $[H_2]$ = 0.15M, $[NH_3]$ = 0.090M. Find K_c at 300°C for reaction.

$$N_2(g) + 3H_2 \rightleftharpoons 2HN_3(g)$$

Solution

K_c is found by simply substituting into the equilibrium equation,

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$= \frac{(0.090)^2}{(0.25)\times(0.15)^3} = 9.6$$

7.4 Applications of Equilibrium Constant Expression

The equilibrium constant can be used to predict;

(*i*) The direction in which a chemical system would proceed to acquire an equilibrium state.

(*ii*) The extent to which a chemical reaction will occur.

(*iii*) The effect of change in conditions upon a chemical system in a state of equilibrium.

7.4.1 Prediction of Direction of Reaction

Often we know the starting concentrations and want to know how much each reactant and each product would be present at equilibrium. For example consider a general gas phase reaction.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

For this

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Here we come across three possibilities when we insert the values of the initial concentrations of the reactants and products in the equilibrium expression.

$$(i) \text{ if } \quad \frac{[\text{initial conc. of C}]^c}{[\text{initial conc. of A}]^a} \times \frac{[\text{initial conc. of D}]^d}{[\text{initial conc. of B}]^b} < K_c$$

In this case, the reaction will proceed in the forward direction *i.e.* from left to right i.e.,

$$aA + bB \longrightarrow cC + dD$$

until equilibrium point is reached.

$$(ii) \text{ if } \quad \frac{[\text{initial conc. of C}]^c}{[\text{initial conc. of A}]^a} \times \frac{[\text{initial conc. of D}]^d}{[\text{initial conc. of B}]^b} > K_c$$

The reaction will proceed to the left *i.e.*,

$$aA + bB \longleftarrow cC + dD$$

so as to attain the equilibrium state.

$$(iii) \text{ if } \frac{[\text{initial conc. of C}]^c}{[\text{initial conc. of A}]^a} \times \frac{[\text{initial conc. of D}]^d}{[\text{initial conc. of B}]^b} = K_c$$

The system is already in equilibrium and the concentration of the reactants and the products remain constant, for the reaction.

$$aA + bB \rightleftharpoons cC + dD$$

Example 2 For the Dissociation of HI

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$K_c = 0.0156$ at 520°C. Predict the direction in which the system will move to attain the equilibrium. The container is of 1 litre capacity in each case.

(*a*) [HI] = 1.00 mole, [H_2] = 0.01 mole, [I_2] = 0.01 mole

(*b*) [HI] = 1.00 mole, [H_2] = 1.00 mole, [I_2] = 1.00 mole

Solution

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = 0.0156$$

(*a*) Initial concentration of HI = 1.0 mole/litre.

Initial concentration of H_2 = 0.01 mole/litre.

Initial concentration of I_2 = 0.01 mole/litre.

Substituting these values in the equation.

$$\frac{[\text{initial conc.}H_2][\text{initial conc.}I_2]}{[\text{initial conc.}HI]^2}$$

$$= \frac{0.01 \times 0.01}{1 \times 1} = 10^{-4}$$

The initial concentration ratio, 10^{-4} is far less than the given value of K_c, 0.0156, hence the reaction will proceed to the right *i.e.*, the direction of the reaction will be.

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

and HI will dissociate further.

(*b*) Initial concentration of HI = 1.0 mole/litre.

Initial concentration of H_2 = 1.0 mole/litre.

Initial concentration of I_2 = 1.0 mole/litre.

Substitute the values in the relation.

$$\frac{[\text{initial conc.}H_2][\text{initial conc.}I_2]}{[\text{initial conc.HI}]^2}$$

$$= \frac{1 \times 1}{1^2} = 1.0$$

The initial concentration ratio 1.0 is greater than the given Kc value 0.0156, hence the reaction will proceed to the left. The direction of the reaction will be.

$$2HI_{(g)} \longleftarrow H_{2(g)} + I_{2(g)}$$

7.4.2 Extent of Chemical Reaction

One of the basic goal of chemistry is to predict the extent to which a chemical reaction can be expected to occur in the laboratory or in nature. A knowledge of the equilibrium constant of the system allows us to make such predictions. As we shall see, the extent of reaction depends upon the magnitude of K_c.

K_c Very Small

Consider the equilibrium system

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ for which the equilibrium constant is 1×10^{-30} at 30°C.

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1 \times 10^{-30} \text{ at } 25°C$$

We note that K_c for this system is very small. An equilibrium mixture of these three gases at 25° will contain very little NO as compared to N_2 or O_2. Suppose, for example that at equilibrium.

$$[N_2] = [O_2] = IM$$

$$\text{Then } [NO]^2 = 1 \times 10^{-30}M,$$

$$\text{or } [NO] = 1 \times 10^{-15}M.$$

We see that concentration of NO in this mixture is very small indeed. This analysis implies that at 250°C the reaction will not occur to any appreciable extent. Only a trace of NO will be formed. The equilibrium mixture will consist almost entirely of unreacted N_2 and O_2. Conversely, if we start with pure NO, the reverse reaction

$$2NO(g) \longrightarrow N_2(g) + O_2(g)$$

will go nearly to completion, virtually all the 'NO' will be converted to N_2 and O_2, when equilibrium is reached

In general, if K_c is very small, the forward reaction (from left to right) will not occur to an appreciable extent and the reverse reaction (right to left) will go nearly to completion.

K_c Very Large

Consider the equilirbium system -

$$2Cl(g) \rightleftharpoons Cl_2(g)$$

$$K_c = \frac{[Cl_2]}{[Cl]^2} = 1 \times 10^{38} \text{ at } 25°C$$

K_c is so large, the equilibrium mixture will consist almost entirely of chlorine molecules. There will be virtually no chlorine atoms.

Suppose, for example, that at equilibrium.

$[Cl_2] = 1M$

then $[Cl]^2 = \frac{1}{1 \times 10^{38}} = 1 \times 10^{-38}$

$[Cl] = 1 \times 10^{-19} M$

The concentration of Cl atoms in this mixture is very small as compared to that of Cl_2 molecules. This argument tells us that at 25°C the reaction, goes virtually to completion. Nearly all the chlorine atoms are converted to chlorine molecules.

$$\text{or } 2Cl(g) \longrightarrow Cl_2(g)$$

Conversely the reaction:

$$Cl_2(g) \longrightarrow 2Cl(g)$$

will not occur to an appreciable extent. Hence Cl is very small as compared to Cl_2 as required by the relation.

$$\frac{[Cl]^2}{[Cl_2]} = 1 \times 10^{-38}$$

In general we can say that in case K_c is very large, the forward reaction from left to right will go nearly to completion.

The reverse reaction, right to left will not accur to an appreciable extent.

K_c is neither very large nor very small

Consider the system

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

for which $K_c = 0.36$ at 25°C

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36 \text{ at } 25^oC$$

Here K_c is close to 1.0. We expect to obtain an equilibrium mixture containing appreciable amounts of both reactants and products. This is true regardless of which side of the equilibrium system we start from. Neither the forward reaction nor the reverse reaction goes to completion:

7.5 Determination of Equilibrium Constant

There are many ways in which we can approach equilibrium position of a chemical reaction. Let us consider the example of dissociation of N_2O_4. Table 7.1 gives the data for three experiments, in which original concentrations are quite different.

Table 7.1

Equilibrium Measurements in the $N_2O_4 - NO_2$ System at 100°C

Expt. No.	Components	Orignial conc. (M)	Equilibrium conc. (M)
I	N_2O_4	0.100	0.040
	NO_2	0.00	0.120
II	N_2O_4	0.00	0.014
	NO_2	0.100	0.072
III	N_2O_4	0.100	0.070
	NO_2	0.100	0.160

Looking at the data in table 7.1 you might wonder whether these three experiments have anything in common. Specially, is there any relationship between the equilibrium concentration of NO_2 and N_2O_4 which is valid for all the experiments?

It turns out that there is, although it is not an obvious one.

The equilibrium constant $K_c = [NO_2]^2/[N_2O_4]$ is the same, about 0.36 in each case

$$\text{Expt. I} \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.120)^2}{0.040} = 0.3600$$

$$\text{Expt. II} \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.072)^2}{0.014} = 0.3703$$

$$\text{Expt. III} \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.160)^2}{0.070} = 0.3657$$

This relationship holds for any equilibrium mixture containing NO_2 and N_2O_4 at 100°C regardless of the fact that from where we start. We find that at equilibrium

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36 - 0.37 \text{ at } (100^{\circ}C)$$

Further experiments with this system at various temperatures lead to the general conclusion that any given temperature the quantity.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \text{ is a constant and is independent}$$

of original amounts of N_2O_4 and NO_2.

7.5.1 Reaction Between an Organic Acid and an Alcohol

Alcohols and acids react to form esters and water. For example

$$\underset{\text{acetic acid}}{CH_3COOH(l)} + \underset{\text{ethyl alcohol}}{C_2H_5OH(l)} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5(l)} + H_2O(l)$$

To find out the value of equilibrium constant K_c, it is necessary to know the equilibrium concentrations at a particular temperature. For this purpose let us take 'a' moles/litre of acetic acid and 'b' moles/litre of ethyl alcohol in a stoppered flask at a particular temperature. After some time equilibrium will be established. The amount of acid present in the equilibrium mixture is found out by titrating it against some standard alkali.

Let the amount of acetic acid present in the mixture at equilibrium be '(a–x)' moles/litre. The amount of acetic acid that had reacted with alcohol therefore would be 'x' moles/litre.

The equation for the reaction indicates that one mole of acetic acid reacts with one mole of alcohol to form one mole of ester and one mole of water. Therefore the amount of alcohol reacted at equilibrium would be 'x' moles/litre, leaving (b–x) moles/litre of alcohol unreacted.

Alternatively, we can write.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initial conc.	'a' mole	'b' mole	zero mole	zero mole
Equilibrium	(a-x) moles	(b-x) moles	x moles	x moles

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{[x][x]}{[a\text{-}x][b\text{-}x]} = \frac{[x]^2}{[a\text{-}x][b\text{-}x]}$$

Example 3

When 60.0g of acetic acid and 46.00g of ethyl alcohol are heated to give an equilibrium mixture, 12.0g of water and 58.7g of ethyl acetate, are formed. Find the equilibrium constant for the reaction.

Solution

In order to take concentration in moles, the amount of each substance present in g is divided by the respective molecular weight.

Initial concentrations:

$$CH_3COOH = 60g = \frac{60g}{60g\ mol^{-1}} = 1\ mol = a$$

$$C_2H_5OH = 46g = \frac{46g}{46g\ mol^{-1}} = 1\ mol = b$$

$$CH_3COOC_2H_5 = 0\ mole$$

$$H_2O = 0\ mol$$

Equilibrium concentrations:

$$CH_3COOC_2H_5 = 58.7g = \frac{58.7g}{88g\ mol^{-1}} = 0.666\ mol = x$$

$$H_2O = 12g = \frac{12g}{18g\ mol^{-1}} = 0.666\ mol = x$$

$$[CH_3COOH] = (a - x) = (1 - 0.666)\ mol = 0.333\ mol$$

$$[C_2H_5OH] = (b - x) = (1 - 0.666)\ mole = 0.333\ mol$$

At equilibrium.

CH_3COOH +	$C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
$a - x$ mol	$b - x$ mol	x mol	x mol
0.333 mol	0.333 mol	0.666 mol	0.666 mol

Therefore equilibrium constant:

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{[x][x]}{[a-x][b-x]}$$

$$= \frac{0.666 \times 0.666}{0.333 \times 0.333}$$

$$= 4$$

Example 4

92.0g of ethyl alcohol was mixed with 120g of acetic acid to give equilibrium mixture. Calculate the amount of ethyl acetate at equilibrium, when $K_c = 4.0$.

Solution

	CH_3COOH +	C_2H_5OH ⇌	$CH_3COOC_2H_5$ +	H_2O
Initial Conc.in garms	120g	92g	0.000g	0.000g
Initial Conc. in mole	$\frac{120g}{60g\ mol^{-1}} = 2$	$\frac{92g}{46g\ mol^{-1}} = 2$	zero mol	zero mol
Equilibrium conc. in mole	(2-x)	(2-x)	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{x.x}{(2-x)\,(2-x)}$$

$$= \frac{x^2}{(2-x)(2-x)}$$

or $$4(x^2 - 4x + 4) = x^2$$

or $$3x^2 - 16x + 16 = 0$$

This is a quadratic equation which can be solved by comparing to the form.

$$ax^2 + bx + c = 0$$

where $a = 3$; $b = -16$, $c = +16$

Applying the quadratic equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

or $$x = \frac{-(-16) \pm \sqrt{(-16)^2 - 4 \times 3 \times 16}}{2 \times 3}$$

or $$x = \frac{+16 \pm \sqrt{256 - 192}}{6}$$

or $$x = \frac{+16 \pm 8}{6}$$

We get x = 1.33 moles or 4.0 moles

The value of x = 4.0 is not possible as it is greater than the concentration of the reactants. Thus, 1.33 moles of ethyl acetate is present at equilibrium.

1 mole of ethyl acetate ($CH_3COOCH_2H_5$) = 88.0g.

Amount of ethyl acetate at equilibrium = 1.33 mole x 88g mol^{-1}

= 117.04g.

Example 5

It is observed that at room temperature the equilibrium constant for

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

is very small. However the equilibrium constant increases with temperature becoming 0.10 at 2000°C. At equilibrium the concentration of N_2 and O_2 was 0.10 M for each.

Calculate the equilibrium concentration of 'NO'.

Solution

The expression for K_c is.

$$Kc = \frac{[NO]^2}{[N_2][O_2]} = 0.10$$

Substituting the values for N_2 and O_2 we get the expression *i.e.*

$$\frac{[NO]^2}{[0.10][0.10]} = 0.10$$

$$[NO]^2 = 1 \times 10^{-3} = 10 \times 10^{-4}$$

$$[NO] = [10 \times 10^{-4}] = 3.162 \times 10^{-2}\ M = 0.032\ M.$$

Example 6 **Consider the system**

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Its K_c = 0.10 at 2000°C. The initial concentration of N_2, O_2 and NO were 0.100 M, 0.100 M and 0.00 M respectively. What are the concentrations of NO, N_2 and O_2 at equilibrium?

Solution

First of all express the equilibrium concentrations of N_2, O_2 and NO in terms of a single unknown x. From the reaction given above it is clear that x moles of N_2 would react with x moles of O_2 to form 2x moles of NO. We can represent *i.e.*

	Initial conc. (M)	Change in conc. (M)	Equilibrium conc. (M)
N_2	0.100	-x	0.100–x
O_2	0.100	-x	0.100–x
NO	0.00	+ 2x	2x

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

or $$0.1 = \frac{(2x)^2}{(0.100-x)(0.100-x)}$$

or $$0.10 = \frac{(2x)^2}{(0.100-x)^2}$$

Taking the square root of both sides.

$$(0.10)^{\frac{1}{2}} = \frac{(2x)}{(0.100-x)}$$

$$= \frac{(2x)}{(0.100-x)} = 0.32$$

or $2x = 0.32\,(0.100-x)$

or $2x + 0.32x = 0.032$

or $2.32x = 0.032$

$$x = \frac{0.032}{2.32} = 0.014$$

From the table above the equilibrium concentrations are i.e. $[NO] = 2x = 0.014 \times 2 = 0.028$ M.

$[N_2] = [O_2] = 0.100 - 0.014 = 0.086$ M.

Note: The above solution of the problem suggests that at 2000°C, significant quantities of NO are formed from N_2 and O_2. This explains why NO resulting from high temperature combustion processes, like the one taking place in automobile engines, is a serious air pollutant.

7.6 Effect of Changes in Conditions Upon an Equilibrium System

Once a system has attained equilibrium, it is possible to change the ratio of products to reactants by changing the external conditions *i.e.* concentration, pressure, temperature and volume. Thus we will consider three ways in which a chemical equilibrium can be disturbed.

(*i*) Adding or removing a reactant or product.

(*ii*) Changing the pressure of the system.

(*iii*) Changing the temperature.

We can deduce the direction in which an equilibrium will shift when one of these changes is made by applying Le-Chatelier's principle which states that *if a system at equilibrium is disturbed by some change, the system will shift so as to counteract the effect of the change.*

We can determine the extent of the shift by working with the equilibrium constant K_c. Let us demonstrate the application of this principle in the following changes.

7.6.1 Adding or Removing a Species — The Effect of Change in Concentration

When the concentration of one or more of the substances, reactants or products present in an equilibrium mixture is disturbed, the system no longer remains in a state of equilibrium. According to Le-Chatelier's principle, the system will undergo changes in concentration of various components, so as to restore the constant value of the equilibrium constant for system. Let us apply this general rule to a chemical system in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Now, if add some more quantity of the substance 'C' to the already established equilibrium as given above then, equilibrium concentration of C will become greater.

In order to keep the concentration ratio $\frac{[C]^c [D]^d}{[A]^a [B]^b}$ equal to K_c, for re-establishing the equilibrium, the concentration of A and B will increase by corresponding amounts until a ratio of concentrations attains a value equal to the equilibrium constant. The following examples shall further illustrate the point

(a) Suppose the following system has reached equilibrium at a certain temperature.

$$N_2O_4(g) \rightleftharpoons 2NO(g)$$

The equilibrium constant of the reaction is given by

$$K_c = \frac{[NO]^2}{[N_2O_4]}$$

We might disturb the equilibrium by:

(*i*) adding N_2O_4. If we do this, the reaction will occur in the forward direction to increase $[NO_2]$. In this way part of the N_2O_4 will be consumed.

(*ii*) adding NO_2, will cause the reverse reaction to occur, to increase the $[N_2O_4]$.

(*iii*) removing N_2O_4 , will cause the reaction to occur in the reverse direction to restore part of the N_2O_4.

(*iv*) removing NO_2, which causes the forward reaction to occur restoring part of the NO_2 removed.

It is possible to use K_c to calculate the extent to which reaction occurs when an equilibrium is disturbed by adding or removing a product or reactant.

(b) Effect of Change in Concentrations in the Formation of NH_3

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

If we want to convert as much hydrogen to ammonia as possible, we must increase the concentration of nitrogen. To understand the effect of this, first suppose that a mixture of nitrogen, hydrogen and ammonia is at equilibrium. If nitrogen is now added to this mixture, the equilibrium is disturbed. According to Le-Chaterlier's principle, the reaction will now go in the direction that will use up some of the added nitrogen.

Consequently, adding more nitrogen than is required by the stoichiometry will have the effect of converting greater quantity of hydrogen to ammonia

(c) Effect of Change in Concentration in the Formation of SO_3

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_c = \frac{[SO_3]^2}{[O_2][SO_2]^2}$$

In this case, addition of more O_2 at equilibrium will increase its concentration above its original equilibrium value. To decrease the concentration of O_2 from the system, the SO_2 and O_2 will react to form SO_3. Thus, as a result of adding more O_2 the concentration of SO_2 is decreased and the concentration of SO_3 is increased and a new position of equilibrium is attained. This means, the addition of more O_2 or SO_2 gas at the equilibrium will result in a greater yield of SO_3.

(d) Formation of NO

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

Here an increase in the concentration of N_2 or O_2 at equilibrium will result in a greater yield of NO.

Example 7

$2HI \rightleftharpoons H_2 + I_2$ is a system at equilibrium at 520°C, where

$$[HI] = 0.080M, \text{ and } [H_2] = [I_2] = 0.010M.$$

To this mixture we add enough HI to raise its concentration temporarily to 0.096M. When equilibrium is restored, what will be the values of [HI], $[H_2]$ and $[I_2]$? The value of $K_c = 0.016$.

Solution

Here the original concentrations are those that prevail immediately after the equilibrium is disturbed.

Original concentration HI = 0.096M.

Original concentrations H_2 = original concentration I_2 = 0.010M.

Since we add HI, some of it must decompose to bring the system back to equilibrium. When that happens some H_2 and some I_2 are formed. Let 'x' be the concentration of H_2 that is produced by this process. H_2 and I_2 are formed in a 1:1 mole ratio, the concentration of I_2 must also increase by 'x'. Again since two moles of HI are required to form one mole of H_2, the concentration of HI must decrease by 2x.

	Original conc. (M)	Change in conc. (M)	Equilibrium conc. (M)
H_2	0.010	+x	0.010+x
I_2	0.010	+x	0.010+x
HI	0.096	−2x	0.096−2x

Substituting into the expression for K_c.

$$0.016 = \frac{(0.010+x)\,(0.010+x)}{(0.096-2x)^2}$$

To solve this equation take the square root of both sides.

Since $(0.016)^{\frac{1}{2}} = \pm\, 0.13$

we have $\pm\, 0.13 = \dfrac{0.010+x}{0.096\text{-}2x}$

Which solves to give an acceptable value of x = 0.002

Thus $[H_2]$ = 0.010 + 0.002 = 0.012M.

$[I_2]$ = 0.010 + 0.002 = 0.012M.

[HI] = 0.096 − 0.004 = 0.092M.

7.6.2 Effect of Pressure Change

A change of pressure on a system in equilibrium can effect the yield of products in a gaseous reaction. When pressure on a gaseous system is increased, the system tends to reduce the volume to undo the effect of increase in pressure. Thus increase of pressure will favour forward reaction. If there is no change in volume during the course of a reaction, the equilibrium will not be changed by change in pressure; since the concentration of the reactants and products are affected in the same proportions.

Consider the following few examples.

(a) Effect of Pressure in the Formation of NO

Consider the reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The reaction shows that there is no change in volume during the formation of NO. Hence there will be no effect of change in pressure on the equilibrium concentrations of reacants and products.

Similarly the following systems will have no effect of any change in pressure, as there is no change of volume in these reactions i.e.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

(b) Effect of Pressure on The Formation of NH_3

$$N_2(g) + 3H_2(g) \xrightleftharpoons{350\text{ atm}} 2NH_3(g)$$

The reaction shows that there is a decrease in volume in the formation of ammonia. Now if pressure is increased on the equilibrium, the reaction shall be favoured to occur in the direction of decrease in volume, i.e., it would result in the formation of more and more ammonia.

(c) Effect of Pressure on the Formation of SO_3

$$2SO_2(g) + O_2(g) \xrightleftharpoons{1.5\text{–}1.7\text{ atm}} 2SO_3(g)$$

As it is evident from the reaction there is a decrease in volume in the formation of SO_3. Hence the formation of SO_3 shall be favoured by an increase in pressure.

(d) Effect of Pressure on the Dissociation of PCl_5

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The reaction indicates that there is an increase in volume in the formation of PCl_3 and Cl_2. The reaction takes place with the increase of number of moles. If pressure is increased at equilibrium stage, reaction is pushed backward and dissociation of PCl_5 is suppressed.

7.6.3 Effect of Temperature Change

Temperature has profound effect on most reactions. According to Le-Chatelier's principle, when a reaction is endothermic i.e. absorbs heat, a rise in temperature will favour

it to proceed to a greater extent. Conversely, the exothermic reactions shall be favoured by lowering of temperature.

Examples

(a) Effect of Temperature on the Synthesis of NH_3

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.38 kJ/mol$$

Since it is an exothermic reaction a low temperature will favour the formation of NH_3. In the industrial manufacture of NH_3 the temperature used is about 450°C.

(b) Effect of Temperature in the Formation of SO_3

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -94.58 kJ/mol$$

It is an exothermic reaction, a low temperature will favour the formation of SO_3. The optimum temperature for this reaction is about 400°C to 450°C.

(c) Effect of Temperature on the Formation of NO

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad \Delta H = 180.5 kJ/mol$$

The formation of 'NO' is an endothermic reaction. Thus according to Le-Chalterlier's principle, a high temperature will favour the formation of NO. Practically the temperature used for its formation on commercial scale is about 3000°C.

7.6.4 Effect of Catalyst on Equilibrium

A catalyst is a substance that affects the rate of a reaction but remains unaltered at the end of the reaction. It is important to know that a catalyst has no effect on the equilibrium composition of a reaction mixture. A catalyst merely speeds up the attainment of equilibrium, by lowering the energy of activation for the reaction (see chapter 9).

7.7 Ionization Constants of Weak Electrolytes in Aqueous Solutions

The process in which the electrolytes and molecules are split up into positively and negatively charge ions is called

ionization. Electrolytes which ionize to a very small extent in a solution are called weak electrolytes.

When a weak electrolyte is dissolved in water only a small amount of molecules is ionized. The ions formed exist in dynamic equilibrium with the undissociated molecules. Thus the equilibrium constant quantitatively measures the extent of ionization or dissociation of an electrolyte.

For example, consider the dissociation of acetic acid in water.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The equilibrium constant for the reaction is given by the expression:

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

$$\text{or } K_c[H_2O] = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Since the concentration of H_2O remains constant in dilute solution, $K_c[H_2O]$ = constant (K_a).

Where K_a is called the dissociation or ionization constant of the acid.

$$\text{Thus} \quad K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.85\times10^{-5} \text{ at } 25^oC$$

7.8.4 Heterogeneous Equilibria

A homogeneous equilibrium is an equilibrium that involves reactants and products in a single phase. On the other hand a heterogeneous equilibrium is an equilibrium involving reactants and products in more than one phase. Some examples of heterogeneous equilibria are given below:

7.8.1 Equilibrium Systems Containing Solid and Gaseous Phases

The reaction of iron metal filings with steam to produce iron oxide Fe_3O_4 and hydrogen is an example of a heterogeneous system.

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe3O_{4(s)} + 4H_{2(g)}$$

In writing the equilibrium constant for a heterogeneous system we omit concentration terms for substances in pure solid phase or in pure liquid phase. Thus for the above reaction we can write:

$$K_c = \frac{[H_2]^4}{[H_2O]^4}$$

The concentration of a pure solid or a pure liquid remains constant at a given temperature while that of a gas varies.

The fact that the concentration of Fe and Fe_3O_4 do not occur in the equilibrium constant expression means that the equilibrium is not affected by the amounts of these susbstances as long as some of each is present.

However chemical equilibrium cannot exist if either Fe or Fe_3O_4 is absent.

$CaCO_3$ decomposes and establishes equilibrium.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

So, $K_c = [CO_{2(g)}]$

or $K_p = p_{CO_2}$

Kp stands for equilibrium constant of this reaction when concentrations are expressed in partial pressures of CO_2.

7.9 Common Ion Effect

The term common ion effect is used to describe the behaviour of a solution in which the same ion is produced by two

different compounds. When a salt is dissolved in a solution that already contains one of its ions, its solubility is less than in pure water.

(*i*) For example, in a solution which contains both calcium oxalate and calcium chloride each salt contributes the same cation Ca^{2+}. The effect of the Ca^{2+} ion provided by the $CaCl_2$ is to make calcium oxalate less soluble than it would be in pure water.

We can explain this decrease in solubility in terms of Le-Chalterlier's principle. Suppose we first mix crystals of calcium oxalate in a given volume of pure water to establish the equilibrium i.e.

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

Now imagine that we add some $CaCl_2$. Since $CaCl_2$ is a soluble salt it dissolves and increases Ca^{2+} ion concentration. We can regard this increase as a stress on the original equilibrium. According to Le-Chealtelier's principle, the oxalate ions will react to remove some of the added Ca^{2+} ion:

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_{4(r)}$$

In other words some calcium oxalate precipitates out from the solution. The solution now contains less $C_2O_4^{2-}$ ions. We conclude that calcium oxalate is less soluble in a solution of calcium chloride than it is in pure water.

In general, an ionic equilibrium is affected by a substance producing a common ion involved in the equilibrium. The effect can be predicated from Le-Chalterlier's principle.

(*ii*) Similarly polassium perchlorate $KClO_4$, is only moderately soluble in water at 25°C. When the very soluble KCl is added to a saturated solution of $KClO_4$, the concentration of common ion K^+ increases and $KClO_4$ precipitates out. The equilibrium is shifted in the backward direction.

$$KClO_{4(s)} \rightleftharpoons K^+_{(aq)} + Cl\bar{O}_{4(aq)}$$

spelling

Le-Chatlier's

Potassium

$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

(iii) Purification of NaCl, in its saturated solution, is carried out by passing HCl gas. Cl^- is a common ion, and the equilibrium shifts to the left whereby NaCl precipitates.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

(iv) The dissociation of H_2S is suppressed by adding dilute HCl because H^+ is a common ion. Only more insoluble sulphides of Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, Sn^{2+} precipitate in II-A and II-B group basic radicals.

$$H_2S_{(g)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

$$HCl_{(g)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

(v) Addition of NH_4Cl in third group of basic radical scheme of qualitative analysis before NH_4OH addition suppresses the ionization of NH_4OH. Less OH^- ions are just sufficient to give precipitates of cations of third group basic radicals (Fe^{3+}, Cr^{3+} and Al^{3+}), which give more insoluble hydroxides.

$$NH_4Cl \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$$

$$NH_4OH \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

EXERCISE

1. Write equilibrium constant expression for each of the following systems:

   (a) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

   (b) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

   (c) $2N_2O_{5(g)} \rightleftharpoons 4NO_{2(g)} + O_{2(g)}$

(d) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O$.

2. Write chemical equations that would lead to each of the following expression for K_c.

(a) $$\frac{[H_2]^2[O_2]}{[H_2O]^2} = K_c$$

(b) $$\frac{[H_2][O_2]^{\frac{1}{2}}}{[H_2O]} = K_c$$

(c) $$\frac{[H_2O]^2}{[H_2]^2[O_2]} = {}_c$$

3. Calculate K_c at 1500°C for the reaction,
$2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
Given that equilibrium concentrations of N_2, O_2 and NO are 0.050M, 0.05M and 0.00055M respectively.
(Ans: 8.26×10^3)

4. For the system
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
K_c = 0.050 at 250°C. In a certain equilibrium mixture at 250°C, $[PCl_3] = 2 \times [PCl_5]$. What is the equilibrium concentration of Cl_2?.
(Ans: 0.025M)

5. Explain what do you understand by the term chemical equilibrium. Give examples.

6. State the law of mass action and derive the equilibrium expression for a general reversible process.

7. Calculate the weight of ethyl acetate formed at 25°C from 100g of C_2H_5OH and 100g of CH_3COOH Kc=4.0.
(Ans: 104.72g)

8. The equilibrium $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 300^oC in a 5.0 litre container has 1.0 mole of NH_3. 0.1 moles of N_2 and 3.0 moles of H_2. Calculate K_c.

(Ans: 9.259)

9. With the help of a chemical equilibrium expression, how will you predict the direction and the extent of a chemical system.

10. Give examples for application of Le-Chalterlier's principle to chemical equilibrium.

11. Predict the effect of raising the temperature upon each of the following gaseous equilibria.

(a) $H_2 + I_2 + \text{Heat} \rightleftharpoons 2HI.$

(b) $2NO + O_2 \rightleftharpoons 2NO_2 + \text{Heat}.$

(c) $2SO_2 + O_2 \rightleftharpoons 2SO_3 + \text{Heat}.$

(d) $N_2 + O_2 + \text{Heat} \rightleftharpoons 2NO$

(e) $CO + H_2O \rightleftharpoons CO_2 + H_2 + \text{Heat}.$

12. Discuss the conditions for temperature, pressure and presence of catalyst suitable for obtaining maximum yields in the following processes.

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) $N_2 + O_2 \rightleftharpoons 2NO$

(c) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

13. Give a brief account of the following.

(a) Heterogeneous equilibria.

(b) Ionization constant of weak electrolytes.

(c) Solubility products.

14. What is common ion effect? Give its applications.

15. The solubility of MgF_2 is 7.6×10^{-2} gdm^{-3}. Calculate K_{sp} for this salt.

Ans. 7.37×10^{-9}m/L.

16. Fill in the blanks with suitable words given in brackets.

(i) There is ____________ equilibrium at constant temperature between liquid and its vapours of a liquid. (static/dynamic)

(ii) It ____________ essential that a reaction may attain equilibrium position after 50% completion. (is/is not)

(iii) Chemical equilibria is concerned with ____________ of the process. (reversibility /irreversibility)

(iv) The rate of a reaction ____________ with the passage of time under given conditions. (changes/does not change)

(v) The equilibrium constant of a reaction is the ratio of two ____________ constants. (rate/equilibrium)

(vi) The forward rate constant of a reaction becomes ____________ with increase of temperature. (greater/slower)

(vii) The equilibrium constant of all the reaction may be ____________ when they are 50% completed. (1/0.5/different)

(viii) The direction and extent of a chemical reaction are told by ____________ constant. (rate/equilibrium)

(ix) The change of concentrations of reactants ____________ the equilibrium constant value permanently (changes/does not change).

(x) The exothermic reactions are ____________ by supplying heat at equilibrium state, but

endothermic reactions are __________.
(favoured/disfavoured)

(xi) A catalyst __________ the rate of forward and __________ the rate of backward reaction. (increase/decrease)

(xii) The numerical value of Kc and Ka for a weak electrolyte is __________. (different/same)

(xiii) The concentration of solids in heterogenous equilibria are considered as __________. (zero/unity/100)

(xiv) Ca^{2+} ions added from out side __________ the ionization of Calcium Oxalate in aqueous solution. (enhances/suppresses)

(xv) The chemical equilibria which includes more than one phase is called __________ equilibria. (static/heterogeneous)

(xvi) That substance which increases the rate of a chemcial reaction but remains uncharged at the end of reaction is called __________. (retrader/ catalyst)

17. Explain the following with reasons:

(i) The rate of decrease of concentration of reactions decreases with the passage of time for a reaction.

(ii) Equilibrium constant is the quantitative measurement of extent of a chemcial reaction.

(iii) The ratio of concentration of reactants and products at equilibrium stage is independent of the directions from where it is started.

(iv) The change of volume changes the equilibrium position only for those reactions in which there

is difference in number of moles of reactants and products.

(v) Exothermic reactions are favoured to the forward direction by cooling at equilirbium stage but endothermic are disfavoured by cooling.

(vi) A catalyst does not change the position of equilibrium but this equilibrium position reaches earlier.

(vii) Le-Chateleir's principle says that solid ice at 0^oC can be melted by applying pressure and without supply of heat from out side.

(viii) Dil. HCl should be added to get the precipitates of II-group basic radicals before passing H_2S gas.

(ix) NH_4Cl is added before NH_4OH to get the precipitates of III-group basic radicals.

8

SOLUTIONS AND ELECTROLYTES

8.1 Introduction

A solution is a homogeneous mixture of two or more than two chemical substances, whose proportion can be varied within certain limits. If the solution is composed of two substances, then it is called a binary solution e.g. a solution of sugar in water.

The substance which is present in large quantity is usually called the solvent and the other is referred to as solute. In 10% aqueous sugar solution, sugar is solute while water is solvent. A solution which contains a relatively small amount of solute dissolved in the solvent is called a dilute solution. On the other hand, a solution which contains a relatively large amount

of solute dissolved in a solvent is called a concentrated solution e.g. 5% aqueous sugar solution is diluter than 10% solution.

A solution can exist in any of the three physical states i.e. solid, liquid or gas. This chapter will emphasise the discussion of a few aspects of aqueous solutions and also the electrolytic behaviour of solutions in general.

8.2 Concentration Units of Solutions

Chemical reactions are frequently carried out in solutions. Since the stoichiometry of chemical reactions is based on relative numbers of reacting atoms, ions or molecules, the designation of concentration units based on the number of solute particles is of particular importance. The amount of solute present in a given amount of solvent or solution is called the concentration of a solution. In applying the concept of the mole to solutions it is necessary to establish fundamental units to be counted. These may be formula units, molecules, atoms or ions.

The amount of solute, solvent and solution may be measured by volume, weight or number of moles. Therefore, concentration of a solution can be expressed in many ways.

(i) Percentage Composition

The composition of a solution based on weight or volume of the components of a solution is easily expressed by percentage composition. The weight of solute present in 100 parts by weight of solution is called weight percentage and the volume of solute present in 100 parts by volume of solution is called the volume percent of solution.

(ii) Normality

Normality is the number of gram-equivalents of solute in a litre of solution.

$$\text{Normality} = \frac{\text{wt. of solute}}{\text{Eq. wt of solute}} \times \frac{1}{\text{Vol. of solution in litres}}$$

(iii) Molarity

The concentration of a solution expressed in moles of solute atoms, ions or molecules per litre of solution is called the molarity. In other words molarity is the number of moles of solute present in one litre of the solution.

Molarity is determined by dividing the weight in grams of solute present in 1 litre by gram molecular weight of the solute.

$$\text{Molarity} = \frac{\text{wt. of solute}}{\text{Mol. Wt. of solute}} \times \frac{1}{\text{Vol. of solution in litres}}$$

or

$$\text{Molarity} = M = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}} \quad \text{.......} \quad (8.1)$$

The symbol for molarity or molar concentration is M.

Example 1

What is the molarity of a solution containing 15.0g urea $CO(NH_2)_2$ in 500.00 ml of solution?

Solution

Converting the amount of solute in grams to moles and volume of solution from millilitres to litres.

$$\text{No. of moles of } CO(NH_2)_2 = \frac{15.0\text{g } CO(NH_2)_2}{60\text{g } CO(NH_2)_2}$$

$$= 0.250$$

$$\text{Volume of solution} = 500.0 \text{ ml}$$

$$= 0.5 \text{ L}$$

$$\text{Molarity of } CO(NH_2)_2 \text{ solution} = \frac{0.250 \text{ moles}}{0.500\text{L}}$$

$$= 0.5 \text{ M}$$

(iv) Molality

Another useful unit is the molality. In this concentration unit, the amount of solute is given in moles and the amount of solvent (not solution) in kilograms. Thus molality is the moles of solute per kilogram of solvent. In other words the molality of a solution is equal to the number of moles of solute dissolved in 1000 g of solvent.

$$\text{Molality} = \frac{\text{Wt. of solute}}{\text{Mol.Wt. of solute}} \times \frac{1}{\text{Weight of solvent in Kg.}}$$

$$\text{or Molality} = m = \frac{\text{Number of moles of solute}}{\text{Number of kilograms of solvent}} \quad ....(8.2)$$

A solution which contains 1 mole of NaCl dissolved in 1000g of water is designated by 1m NaCl. Similarly 1.0 molal solution of glucose contains one gram molecular wieght (180g) of glucose per 1000g of solvent and 0.1 molal solution of it will contain one tenth of its gram molecular weight (18g) in 1000g of the solvent.

Molality of the solution is independent of temperature.

(v) Mole Fraction

The idea of mole fraction is more useful when the components of the solution are more than two. Mole fraction is the ratio of the number of moles of a particular component of the solution to the total number of all the components of the solution.

$$\text{Mole fraction} = \frac{\text{Moles of the component}}{\text{Total moles of all the components of the solution}}$$

For a solution of three components

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3}, \quad X_2 = \frac{n_2}{n_1 + n_2 + n_3}$$

For example

$$Ag_2Cr_2O_7 \rightleftharpoons 2Ag^+ + Cr_2O_7^{-2}$$

$$K_{sp} = [Ag^+]^2 [Cr_2O_7^{-2}]^1$$

Its value is 1.9×10^{-12}

Applications

The solubility product principle may be used to predict whether precipitation will occur or not under given concentration.

We have seen that the numerical value of the solubility product of a salt gives a quantitative limit of the solubility of the salt. For a particular solution of a salt the product of concentrations of ions each raised to the appropriate power is called the ionic product. For a saturated solution in equilibrium with excess solid the ionic product equals the K_{sp}. If the ionic product of a solution is less than the K_{sp}, the solution is unsaturated. Additional solid can dissolve in this solution. On the other hand, if the ionic product is greater than the K_{sp}, the solution is momentarily supersaturated and the precipitation will occur until the ionic product becomes equal to the K_{sp}.

Example 2

The solubility product of $PbCl_2$ at 25°C is 1.7×10^{-5}. Calculate the concentration of Pb^{+2} in solution when solid $PbCl_2$ is added to distilled water.

Solution

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \text{ but } [Pb^{2+}] = \frac{[Cl^-]}{2}$$

or $[Cl^-] = [2Pb^{2+}]$

or $K_{sp} = [Pb^{2+}][2Pb^{2+}]^2 = 4[Pb^{2+}]^3$

or $\frac{K_{sp}}{4} = [Pb^{2+}]^3$

or $[Pb^{2+}] = \sqrt[3]{\frac{K_{sp}}{4}}$

Thus $[Pb^{2+}] = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}}$

$= 1.62 \times 10^{-2}$ g ions /litre

Example 3

A saturated solution of BaF_2 at 25°C is 0.0065M. Calculates K_{sp}.

Solution

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

$$[Ba^{2+}]\,[F^-]^2 = K_{sp}$$

Since a saturated solution of the completely ionized salt is 6.5×10^{-3}M, the concentration of Ba^{2+} is 6.5×10^{-3}M, and that of F^- is twice as much i.e. $[F^-] = 1.3 \times 10^{-2}$M, because according to the equation, two F^- ions are produced for every BaF_2 which dissolves. Substituting these values in the equation for solubility product, we get

$$Ksp = (6.5 \times 10^{-3})\ (1.3 \times 10^{2-})$$

$$= 1.1 \times 10^{-6}$$

8.5 Theory of Ionization

In order to account for the conductivity of electrolytes, electrolysis and certain properties of electrolytic solutions, Arrhenius in 1884 advanced a theory of electrolytic dissociation. According to this theory.

(i) Acids, bases and salts when dissolved in water yield two kinds of particles, called ions. One carries

positive charge and the other carries negative charge. Ion is a Greek word which means wanderer. The positively charged ions are called the cations and negatively charged ions are called the anions.

$$NaCl \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

These ions can move freely in the solution in any direction.

(ii) Ions in the solution also recombine with each other to form neutral molecules and this process continues till an equilibrium state between an ionized and unionized solid is attained.

$$NaCl \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Ionization is thus a reversible process. To this process, the law of mass action can be applied as

$$K_c = \frac{[Na^{+}]\,[Cl^{-}]}{[NaCl]}$$

Where the square brackets [ ] show the equilibrium concentration of the ions and the unionized molecule expressed in moles per litre and K_c signifies the ionization constant.

(iii) When an electric current passes through the solution of an electrolyte the positive ions i.e., the cations move towards the negatively charged electrode called cathode. The negative ions i.e., anions move towards the positively charged electrode called anode. It is this movement of ions that is responsible for the conduction of electricity in solutions of electrolytes. The ions exist in solution in random motion before the current is passed. Their movement towards the oppositely charged electrodes takes place under the effect of emf and the chemical reactions take place at

the electrodes. This explains the process of electrolysis.

(iv) The degree of dissociation i.e., the fraction of the total number of molecules present in the ionic state depends upon (a) the nature of the electrolyte (b) the dilution of the solution (c) the temperature. The more dilute the solution and higher the temperature, the greater is the degree of dissociation. Complete dissociation is attained only at an infinite dilution.

(v) The electrical conductivity of the solution of an electrolyte depends upon the number of ions present in the solution, which are proportional to the degree of dissociation of an electrolyte at a particular concentration and the temperature.

Note:- Certain electrolytes like acids e.g., HCl, H_2SO_4, HNO_3, CH_3 COOH etc., are not ionized in the pure state. They can only form ions when dissolved in water. In water they react to form ions. For example,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The H_3O^+ ions are also called hydronium ions. They are present in aqueous solution of acids and are responsible for their characteristic acid properties.

8.6 Conductance of Electricity Through Aqueous Solutions of Electrolytes

Aqueous solutions of all electrolytes (acids, bases and salts) conduct electricity. They also decompose during this process. The process whereby an electric current is used to bring about chemical reactions that do not take place spontaneously is called electrolysis. The amount of chemical change produced by an electric current is directly proportional to the quantity of electricity passed. This fact is known as Farday's first law of electrolysis.

Let us study the conductance of electricity through an aqueous solution of an electrolyte such as sodium chloride.

An electrolytic cell is shown in Fig. 8.1. A beaker with two inert electrodes and a source of electric potential i.e. direct current (D.C.) constitutes an electrolytic cell. When a solution of concentrated sodium chloride, NaCl is placed in the cell and the

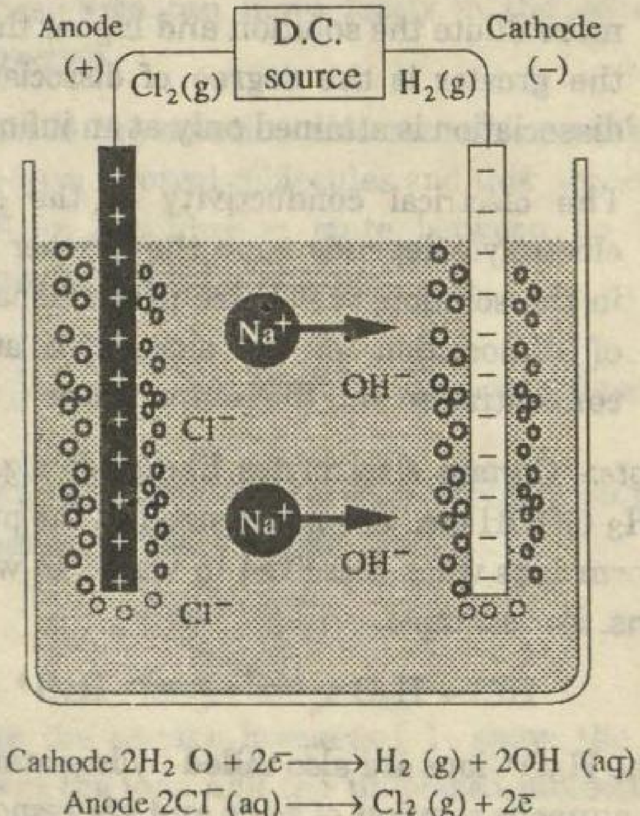


Fig. 8.1 — Electrolysis of Sodium Chloride solution in water

$$\text{Cathode} \quad 2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-_{(aq)}$$

$$\text{Anode} \quad 2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

electrodes are connected to a source of D.C., we find that hydrogen gas (H_2) is produced at the cathode while chlorine gas (Cl_2) is produced at the anode. At the same time the solution in the cell becomes basic. How can we explain these observations?

Solid sodium chloride when dissolved in water dissociates into ions.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

The following reaction occurs at the anode

$$2Cl^-_{(g)} \longrightarrow Cl_{2(g)} + 2e^- \text{ (oxidation reaction)}$$

It may be noted that at the cathode Na^+ is not reduced to metallic sodium. Instead gaseous hydrogen and OH^- ions are produced at the cathode by the reduction of water. The reaction at the cathode can be represented as

$$2H_2O_{(\ell)} + 2e^- \longrightarrow 2OH^-_{(aq)} + H_{2(g)} \text{ (reduction reaction)}$$

The net reaction in the cell can be written as

$$\underset{(2NaCl)}{2H_2O + 2Cl^- + 2Na^+} \longrightarrow \underset{(2NaOH)}{2OH^- + H_2 + Cl_2 + 2Na^+}$$

The above explanation indicates that in fact two separate reactions take place in the electrolytic cell. The reaction at the anode involves removal of electrons which is also called oxidation. It represents only half of the net reaction. It is, therefore, also called oxidation half reaction. The reaction at the cathode involves addition of electrons which is also called reduction half reaction. The net reaction which involves both oxidation and reduction is called the 'redox' reaction. Remember the reduction always takes place at the cathode and oxidation always takes place at the anode. The current through the solution of an electrolyte is due to the movement of ions as shown in Fig. 8.1. It is also clear that H_2O is more easily reduced than Na^+.

The solution that remains in the cell contains sodium hydroxide, NaOH which is a base. The electrolysis of sodium chloride solution in water is used as an industrial process for the production of caustic soda.

8.7 Electrolysis of Fused Sodium Chloride

When current is passed through fused (molten) sodium chloride placed in an electrolytic cell then chlorine is produced at the anode and molten sodium metal is produced at the cathode. Fig. 8.2.

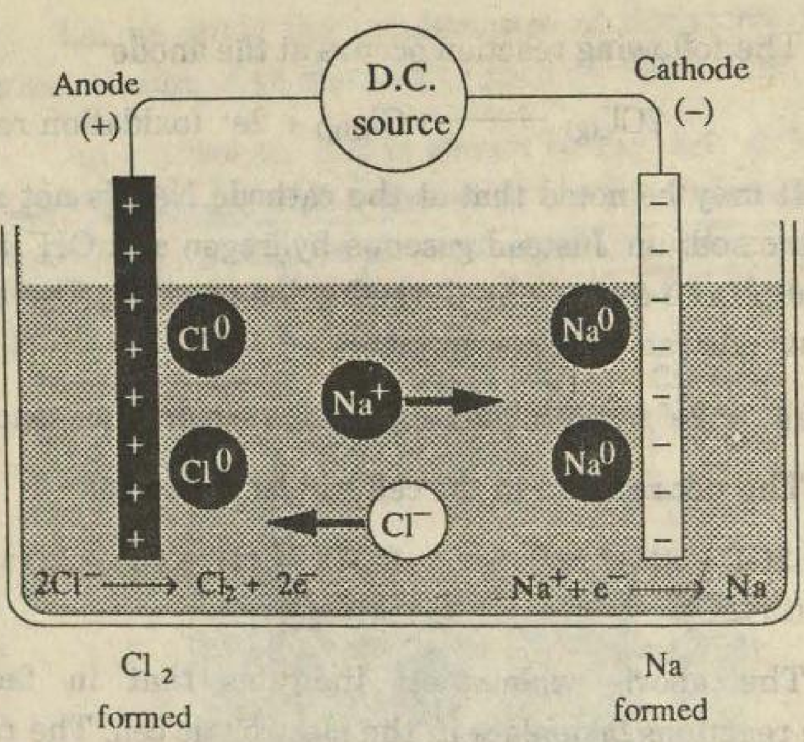


Fig. 8.2 — Electrolysis of fused sodium chloride

The reaction can be represented as under

Ionization:

$$NaCl_{(s)} \longrightarrow Na^+ + Cl^-$$

Oxidation half reaction at anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Reduction half reaction at cathode

$$2Na^+ + 2e^- \longrightarrow 2Na$$

The net redox reaction can be written as

$$2NaCl \longrightarrow Cl_2 + 2Na$$

Sodium metal is collected at the cathode while chlorine gas evolves at the anode.

8.8 Galvanic or Voltaic Cells

In the previous section we studied the process of electrolysis in which the flow of electrons due to an electric potential placed across the electrodes forced non-spontaneous chemical reactions to take place. Now we turn to the opposite

situations in which spontaneous chemical reactions of oxidation and reduction produce potential across the electrodes and if the electrodes are connected by a wire the electrons begin to flow through it producing electric current. A cell in which a redox reaction produces an electric current is known as a galvanic or a voltaic cell. First let us study a spontaneous redox reaction.

When a zinc plate is placed in a solution of copper sulphate, a dark brown layer of metallic copper begins to form on the zinc plate. At the same time it is observed that the blue colour of copper sulphate begins to fade in the solution. If we analyse this solution we find that zinc ions are present in the solution. This reaction can be expressed by a chemical equation as given below:

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

This reaction can be divided into the following two redox half reactions.

$$Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^- \qquad \text{oxidation half reaction}$$

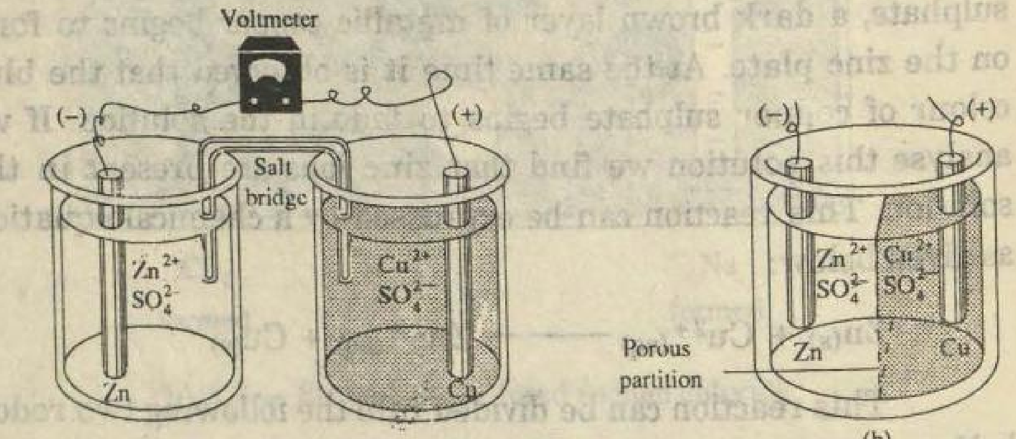
and

$$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{reduction half reaction}$$

The overall reaction involves the transfer of electrons from zinc, $Zn_{(s)}$ to copper ions $Cu^{2+}{}_{aq}$. As long as the reaction takes place on the surface of zinc electrode placed in copper sulphate solution, the reaction simply generates heat and no useful work can be obtained by the transfer of electrons from zinc to copper ions.

However we can carry out the oxidation half reaction and reduction half reaction in separate compartments of the galvanic cell as well, as shown in Fig. 8.3(a). In this figure, a zinc, (Zn) electrode is placed in a solution of zinc sulphate, ($ZnSO_4$) and a copper (Cu) electrode is placed in a solution of copper sulphate ($CuSO_4$). The two solutions are connected by a salt bridge. A salt bridge is U shaped tube filled with an electrolyte such as KCl in gelatin. A salt bridge serves three purposes (a) it allows electrical contact between two solutions

(b) it prevents mixing of the electrode solutions and (c) it maintains electrical neutrality in each half cell. A porous partition can also serve the same purpose, Fig. 8.3(b).



(b)

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e \qquad Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

(a)

Fig. 8.3 -- Zinc-copper galvanic (voltaic) cell.
(a) cell with salt bridge (b) cell with porous partition.

The electrodes are connected by a wire and a voltmeter is inserted in the circuit to measure the potential difference between the two electrodes.

When the circuit is completed the electrons flow in the wire from Zn electrode to the Cu electrode where Cu^{2+} ions from the solution pick up the electrons to become copper atoms. The electrons flowing in the external wire constitute an electric current and the galvanic cell serves as a source of electricity.

The flow of electrons in the wire, or in other words the electrical current grenerated in a galvanic cell is the result of electrons being pushed or forced to flow from the negative electrode, through the wire, into the positive electrode. This force is called the electromotive force or emf and is measured in

volts (V). Actually the volt is a measure of the energy that is capable of being extracted from the flowing electric charge. If the emf is 1V and the charge passed is 1 coulomb the work done is equal to 1 joule.

$$IV \times IC = 1J$$

The emf produced by a galvanic cell is known as the cell potential, E_{cell}. This emf depends on the nature and concentrations of ions, the temperature and the partial pressures of any gases that might be involved in cell reactions. When the concentrations of ions are 1M, the temperature is 25°C and the partial pressures of gases is 1 atm, the cell potential is known as standard cell potential and is denoted by E^0_{cell}.

The electrode at which the oxidation reaction takes place is called the anode and the one at which the reduction takes place is called the cathode. In the cell discussed above Zn electrode is the anode and Cu electrode is the cathode.

8.8.1 Electrode Potential

In the study of a cell, we observed that cell reaction consists of two parts and hence the cell may be regarded as composed of two half-cells, each containing an electrode. In each half-cell, there exists a tendency to acquire electrons from its respective electrode and ions are reduced. In other words each reduction half-reaction has a tendency to proceed from left to right that can be described by its reduction potential.

$$Zn^{2+}{}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$

and

$$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The larger the reduction potential, the greater is its tendency to undergo reduction. In the zinc-copper cell, therefore, copper must have a larger reduction potential than zinc because copper is reduced.

The potential that we measure for a cell is the difference in the tendencies of two ions to get reduced. It is equal to the reduction potential of the substance that actually undergoes reduction minus the reduction potential of the substance that is forced to undergo oxidation. In terms of standard reduction potentials the E^o_{cell} of cell is given by

$$E^o_{cell} = E^o_{substance\ reduced} + E^o_{substance\ oxidized}$$

8.8.2 Standard Hydrogen Electrode (SHE)

Since the voltage created by a cell is actually the difference between the reduction potentials of the two half reactions, it would be useful to construct a table showing the reduction potentials for different half reactions. In fact there is no method of determining the single reduction potential. However, the potential of a single electrode can be measured by coupling it with a standard half cell whose electrode potential (reduction potential) has been assigned a convenient value. The electrode chosen as a standard for the determination of half cell potential is a hydrogen electrode.

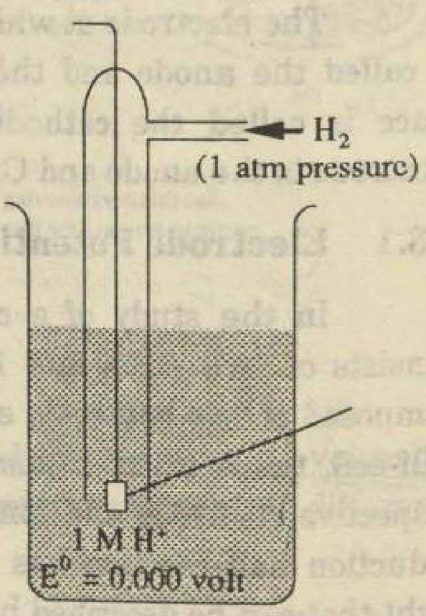


Fig. 8.4 — Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode, Fig. 8.4 consists of a platinum foil that is coated with a layer of finally divided platinum. This foil is connected with a platinum wire and encased with a glass sleeve with hydrogen gas passing through it at pressure of 1 atm. It is then immersed in 1 M HCl solution.

The electrode potential (oxidation or reduction) of the standard hydrogen electrode is arbitrarily chosen as zero at all temperatures.

SHE half-reaction

$H_2 \longrightarrow 2H^+ + 2e^-$ .... exactly 0.000 V SHE as anode

$2H^+ + 2e^- \longrightarrow H_2$ .... exactly 0.000 V SHE as cathode

The apparatus for measuring standard reduction potential by SHE is shown in Fig. 8.5.

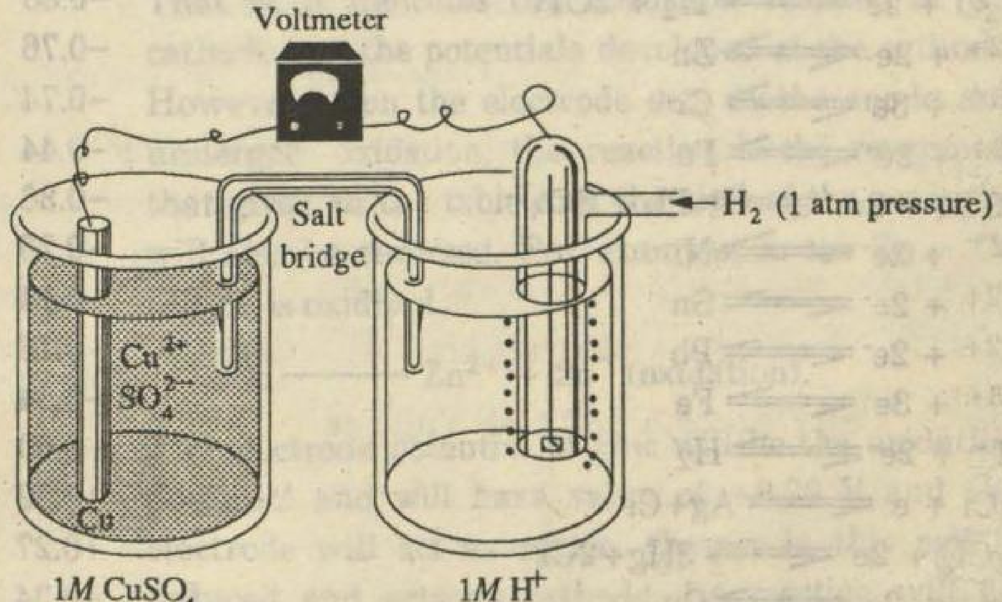


Fig. 8.5 — Apparatus for measuring standard reduction potentials

When a cell is constructed of a standard hydrogen electrode and some other standard electrode (half-cell), then the standard cell potential, E^o_{cell}, is arbitrary taken as the standard potential of the other electrode. By measuring the potentials of other standard electrodes versus the SHE we can develop a series of standard reduction potentials. This series is given is in Table 8.1.

TABLE 8.1
Standard Reduction Potentials at 25°C

Reduction Half-reaction	E° (volts)
$Li^+ + e^- \rightleftharpoons Li$	–3.05
$K^+ + e^- \rightleftharpoons K$	–2.92
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.76
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.67
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.03
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$	–0.36
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$AgCl + e^- \rightleftharpoons Ag + Cl^-$	+0.22
$HgCl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+0.27
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	+0.788
$Ag^+ + e^- \rightleftharpoons Ag$	+.080
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.09
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.36

Reduction Half-reaction	E° (volts)
$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^+ + MnO_4^- + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{2-} + 4H^+ + 4e^- \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.78
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.00
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87

In using the reduction potentials given in this table, the following points must be kept in mind.

(i) The table shows the standard reduction potentials. That is, it indicates the reduction reaction at the cathode and the potentials developed at the cathode. However when the electrode acts as the anode and undergoes oxidation, the reaction is the reverse of that given in the table and the sign of the potential will also be reversed. For example, in the Zn – Cu cell Zn is oxidized.

$$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (oxidation).}$$

The electrode potential of zinc will be the oxidation potential and will have value of +0.76 V and the electrode will act as anode. Copper in this cell is reduced and acts as cathode. Its reaction will be written as

$$Cu^{++} + 2e^- \longrightarrow Cu \text{ (reduction)}$$

and the electrode potential will be reduction potential equal to +0.34.

(ii) Whether or not the cathode reaction will occur spontaneously when the electrode is connected to a hydrogen electrode can be inferred from the sign of the reduction potential in the table. If the sign is positive the reaction will occur as given in table 8.1. The electrode will act as the cathode and the

hydrogen electrode as the anode. If the sign is negative the reaction will occur spontaneously in the opposite direction and the hydrogen electrode will act as the cathode. For example, as the sign of electrode potential in case of Zn is negative with respect to hydrogen the reactions in Zn – H_2 cell will occur spontaneously as under:

$$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (oxidation)}$$
$$2H^+ + 2e^- \longrightarrow H_2 \text{ (reduction)}$$

(iii) When a hydrogen electrode acts as the cathode the reaction is

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (reduction)}$$

But when it acts as the anode the reaction is

$$H_2 \longrightarrow 2H^+ + 2e^- \text{ (oxidation)}$$

(iv) The reduction potentials increase from −3.04 V for Li to +2.87 V for F_2. This means that there is an increasing tendency from top to bottom to gain electron i.e. to undergo reduction and a decreasing tendency to lose electrons, i.e., to undergo oxidation.

8.9 Cell Reaction and Cell Voltage

Table 8.1 can be used to predict the reaction and voltage of any cell that consists of any two standard electrodes. The cell reaction is the algebraic sum of the reactions of the half reactions taking place at the electrodes. For example in the Daniell cell, which is a Zn-Cu cell the two half reactions and the cell reaction are indicated as under:

$$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (oxidation half-reaction at anode)}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \text{ (reduction half-reaction at cathode)}$$
$$\overline{Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \text{ (cell reaction)}}$$

The representation of cells and cell potentials follow certain conventions. According to these conventions the anode at which oxidation takes place (higher in Table 8.1) is represented

on the left hand side along with its ions in solution and cathode at which reduction takes place (lower in Table 8.1) is represented on the right hand side along with its ions in solution. The two half cells are separated by two vertical parallel lines which indicate the salt bridge as indicated below:

electrode' ions in solution || ions in solution' electrode

anode, (oxidation)	cathode, (reduction)
[higher in Table 8.1]	[lower in Table 8.1]

For example the standard Zn–Cu cell will be represented as under:

$$Zn, Zn^{2+}\ (1.0M)\ ||\ Cu^{2+}\ (1.0M)'\ Cu$$

Accordingly the Pb–Cu standard cell will be represented as:

$$Pb, Pb^{2+}\ (1.0M)\ ||\ Cu^{2+}\ (1.0M)'\ Cu$$

It indicates that Pb acts as anode and is being oxidized and Cu acts as cathode and is being reduced.

When cells are represented as above, the cell voltage E^o_{cell} is given by the algebraic sum of the oxidation potential and reduction potential.

$$E^o_{cell} = E^o_{ox} + E^o_{red} \quad .... (8.4)$$

convention

Example 4

Represent in the conventual manner the voltaic cells in which each of the following reactions occur spontaneously.

(i) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

(iii) $Pb + 2Ag^{+} \longrightarrow Pb^{2+} + 2Ag$

Also calculate their E^o_{cell} values. Their standard reduction potential values are:

Zn^{2+}/Zn^0	-0.76v
Cu^{2+}/Cu^0	+034v +0.34V

Al^{3+}/Al^{0}	+1.67v
$Cl_2/2Cl^-$	+1.36v
Pb^{2+}/Pb	−0.13v
Ag^{+1}/Ag^{0}	+0.80v

Solution:

(i) $Zn, Zn^{2+} \; || \; Cu^{2+}, Cu$

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

$$= E^o_{Zn/Zn^{o2+}} + E^o_{Cu^{+2}/Cu^0}$$

$$= 0.76\text{ V} + 0.34\text{ V}$$

$$= 1.10\text{ V}$$

Remember E^o_{ox} is equal to E^o_{red} but reverse in sign.

Similarly *(ii)* can be written as.

(ii) $Al; Al^{3+} \; || \; Cl^-; Cl_2$

$$E^o_{cell} = E^o_{Al/Al^{3+}} + E^o_{Cl/Cl_2}$$

$$= 1.67\text{ V} + 1.36\text{ V}$$

$$= 3.03\text{ v}$$

and

(iii) $Pb; Pb^{2+} \; || \; Ag^+; Ag$

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

$$= E^o_{Pb/Pb^{2+}} + E^o_{Ag^+/Ag}$$

$$= 0.13\text{ V} + 0.80\text{ V}$$

$$= 0.93\text{ V}$$

8.10 Oxidation Number and Oxidation State

The oxidation number is defined as the apparent charge, positive or negative, which an atom would have in a compound. It can also be referred to as oxidation state. It differs from the valence of an ion because the valence is mere number and does not indicate the positive or negative character of the atoms.

The oxidation state of an element or radical is described by its oxidation number which is assigned according to the following rules.

Rules for Assigning Oxidation Number

1. The oxidation number of a free element is zero.
2. The oxidation number of hydrogen is + 1 in its compounds except in the case of metal hydrides, when it is − 1.
3. The oxidation number of oxygen is −2 except in the case of peroxides when in is −1. Another exception is the case of OF_2 in which oxygen is in +2 state.
4. The oxidation number of each element of group VII-A halogens, in binary compounds is −1 i.e., Cl in HCl, Br in $CaBr_2$ and I in KI have −1 oxidation numbers.
5. The oxidation number of each element of the group I-A, II-A and III-A are +1 +2, and +3 respectively.
6. The total oxidation number in any species is the charge of the species. The total charge of the compound is zero and the charge of an ion is equal to the total charge of the oxidation numbers of the elements making up the ion.
7. The guiding principle in assigning oxidation numbers is based on the difference of electronegativity. The more electronegative element controls the electrons shared with another atom.

For example, the oxidation number of Mn in $KMnO_4$ can be determined as indicated below:

$KMnO_4$

1 K atom = +1
4 O atoms = −8

= −7

In order to balance the -7 charges, the Mn is in +7 state.

8.11 Balancing Redox Equations by Oxidation Number Method

The key to balance redox equations is the electron transfer. The number of electrons gained by the oxidizing agent must be equal to the number of electrons lost by the reducing agent. The rules for balancing are few but are important.

(i) Write the formulae for the principle reactants and products.

(ii) Spot the elements which undergo a change in oxidation number and write their oxidation numbers over the symbols.

(iii) Indicate the number of electrons gained or lost by means of arrows.

(iv) Determine the least common denominator for the number of electrons gained and lost and co-efficients needed to yield this number of electrons.

(v) Balance the principle reactants and products using the coefficients given by rule *(iv)*, as above.

(vi) Balance the rest of the equation by inspection method. Finally balance hydrogen and oxygen by putting water when ever needed.

Example 5

Balance the following equation by oxidation number method:

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

Solution

In this equation nitrogen is reduced from +5 in HNO_3 to +2 in NO. It should also be noted that in the $Cu(NO_3)_2$, there are two nitrogen atoms that are not reduced. For this reason, it is convenient to write the equation with HNO_3 in two places.

The HNO_3 in one place is used for the redox reaction while the HNO_3 in the other position is not reduced. Thus the equation may be written as:

$$HNO_3 + \underset{}{Cu^o} + \underset{(5^+)}{HNO_3} \xrightarrow{\text{loss of } 2e^-} Cu(NO_3)_2 + \underset{\text{gains } 3e^- \quad (2^+)}{NO} + H_2O$$

Balance the gain or loss of electrons by balancing the principle products and reactants.

$$HNO_3 + 3Cu + 2HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Balancing the unreacted HNO_3 by inspection. Six NO_3 groups are needed for the $3Cu(NO_3)_2$ and require $6HNO_3$.

$$6HNO_3 + 3Cu + 2HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + H_2O$$

or

$$8HNO_3 + 3Cu \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

8.12 Balancing of Equations by Ion-Electron Method

The ion electron method works on the principle of equalizing the number of electrons lost by the reducing agent and gained by the oxidizing agent.

The ion electron method deals with those ions which actively take part in the oxidation and reduction process and eliminates all the unnecessary ions. The rules regarding the balancing of an ionic equation by this method are given below:-

(i) Write two half reactions one for oxidation process, the other for reduction process. Balance each of the half reactions.

(ii) Add H_2O and H^+ or OH^- to either side of each of the half reactions to balance O and H atoms. It should be remembered that H_2O and H^+ are added if the medium is acidic. For basic media, H_2O and OH^- are added. Further electrons are added to balance the charges.

(iii) Determine the least common denominator of electrons gained and lost, then multiply each half reaction by the appropriate number to affect a balance of electrons transferred. When the two are added the electrons cancel out.

(iv) Add half reactions, simplify the sum of half-reactions in order to obtain the net ionic equation.

Example 6

Balance the following equation by ion-electron method.

$$MnO^{-}_{4} + SO_2 \longrightarrow SO_4^{2-} + Mn^{2+}$$

Solution

(i) Write the two half reaction, one as oxidation half and other as reduction half reaction.

$SO_2 \longrightarrow SO_4^{2-}$ .... (i) oxidation half reaction

$MnO_4^{-1} \longrightarrow Mn^{2+}$ ..... (ii) reduction half reaction

(ii) Balance number of O atoms by adding two H_2O molecules on left of eq (i) and than balance 4 H-atom by adding $4H^+$ on right of it.

$2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+$ .... (iii)

(iii) Add $2e^-$ on right of eq (iii) to balance the charges.

$2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ .... (iv)

(iv) Balance oxygen atoms in reduction half reaction by adding $4H_2O$ on right hand side of (ii), then add $8H^+$ on left to balance H-atoms and then $5e^-$ on left to balance the charges.

$5e^- + 8H^+ + MnO_4^{1-} \longrightarrow Mn^{2+} + 4H_2O$ .... (v)

(v) Now multiply each half reaction by an appropriate number so that the number of electrons on both the half reactions become equal and then add the two reactions. Multiply (iv) by 5 and (v) by 2.

$$5(SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-)$$

$$2(MnO_4^{1-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

$$5SO_2 + 10H_2O + 2MnO_4^- + 16H^+ \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 8H_2O + 20H^+$$

Simplify by cancelling excess H_2O and H^+

$$5SO_2 + 2H_2O + 2MnO_4^- \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

8.13 Hydrogen Ion Concentration, pH

Pure water feebly ionizes into hydrogen and hydroxyl ions as

$$2H_2O \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant expression is given by the equation

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O]$ is in large excess and remains constant. Thus the above equation can be expressed as

$$K[H_2O] = [H^+][OH^-]$$

or $\quad K[H_2O] = K_w = [H^+][OH^-]$ ....(8.5)

Where K_w is called the ionic product of water. The value of the ionic product at 25°C has been found by conductivity measurements to be 10^{-14}. Since water being neutral in character, yields on dissociation an equal number of hydrogen and hydroyl ions. We may therefore write,

$[H^+][O\bar{H}] = 10^{-14}$ ....(8.6)

and $\quad [H^+] = [O\bar{H}] = 10^{-7}$

A solution which contains hydrogen ion concentration equal to 10^{-7}M is said to be neutral. If the hydrogen ion concentration is greater than 10^{-7}M, the solution is said to be acidic whereas if the concentration is less than10^{-7}, the solution is basic. Thus the concentration of hydrogen ion is a measure of the acidity or alkalinity of a solution. Consider an aqueous solution containing 1M HCl. The concentration of H^+ and OH^- ions in an aqueous solution can vary from 1 to 10^{-14} mole/litre. Sorensen suggested a convenient method of expressing the concentration of hydrogen ions in terms of pH. The pH of a solution may be defined as the logarithm of the reciprocal of the hydrogen ion concentration or negative logarithm of hydrogen ion concentration.

Mathematically

$$pH = \log \frac{1}{[H^+]}$$

or

$$pH = -\log [H^+] \text{ ....(8.7)}$$

Similarly, pOH which expresses the hydroxyl ion concentration of solution is given by

$$pOH = \log \frac{1}{[OH^+]}$$

$$= -\log [OH^-] \text{ ....(8.8)}$$

Upon taking logarithm of equation (8.6) and changing the signs throughout it is seen that

$$-\log [H^+] - \log [OH^-] = 14$$

or $$(-\log [H^+]) + (-\log [OH^-]) = 14$$

$$pH + pOH = 14 \text{ ....(8.9)}$$

The sum of pH and pOH is thus equal to 14 for water at 25°C. The relationship between hydrogen and hydroxyl ion concentration and pH and pOH of certain aqueous solutions are given in the Table 8.2.

Table 8.2

The pH Scale

pH	$[H^+]$	$[OH^-]$	
14	10^{-14}	10^{0}	↑
13	10^{-13}	10^{-1}	
12	10^{-12}	10^{-2}	increasing
11	10^{-11}	10^{-3}	alkalinity
10	10^{-10}	10^{-4}	
9	10^{-9}	10^{-5}	
8	10^{-8}	10^{-6}	
7	10^{-7}	10^{-7}	Neutrality
6	10^{-6}	10^{-8}	
5	10^{-5}	10^{-9}	
4	10^{-4}	10^{-10}	
3	10^{-3}	10^{-11}	
2	10^{-2}	10^{-12}	Increasing
1	10^{-1}	10^{-13}	acidity
0	10^{0}	10^{-14}	↓

Thus we see that the pH lower than 7 indicates an acid solution (high hydrogen ion concentration) while a high pH indicates a basic solution (low hydrogen ion concentration) and the scale of pH lies between 0 to 14.

Example 7

What is the pH of a solution for which $[OH^-] = 0.15M$.

Solution

$$[OH^-] = 1.5 \times 10^{-1}$$

$$\log [OH^-] = \log 1.5 + \log 10^{-1}$$

$$= 0.2 - 1.0 = -0.8$$

Since $pOH = -\log [OH^-]$

$$pOH = 0.8$$

$$pH = 14 - 0.8 = 13.2$$

An alternate solution is as under:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H^+] = \frac{10 \times 10^{-15}}{1.5 \times 10^{-1}} = 6.7 \times 10^{-14}$$

$$\log [H^+] = \log 6.7 + \log 10^{-14}$$

$$= \log 6.7 - 14 \log 10$$

$$-\log [H^+] = -\log 6.7 + 14 \log 10$$

$$= -0.8 + 14 = +13.2$$

Thus $pH = 13.2$

Example 8

What is the $[H^+]$ of a solution with a pH of 10.6

Solution

$$-\log [H^+] = -10.6 = 0.4 - 11.0$$

Taking anti log

$$[H^+] = \text{anti log } 0.4 \times \text{anti log } (-11)$$

$$[H^+] = 2.5 \times 10^{-11}$$

Example 9

Calculate the pH of 0.001 M HCl

Solution

Since HCl ionizes completely in water the hydrogen ion concentration is 0.001 moles/litre. = 10^{-3}M

$$\text{Therefore pH} = \log \frac{1}{[H^+]} = -\log [H^+]$$

$$pH = -\log 10^{-3} = -(-3) \times \log 10$$

Since $\log 10 = 1$

Therefore $pH = -(-3) = 3$

8.13.1 Determination of the pH of a Solution

Two methods are frequently used to determine the pH of a solution. They are

1. By the use of an indicator
2. By electrometric method.

1. The indicators may be used in liquid form or as indicator papers. The indicator papers commonly called pH papers, are available commercially. Indicators cannot however be used in case of coloured solutions.
2. The electrometric method of determining pH specially that involving the use of a glass electrode is the more accurate method. In this case the potential difference generated across a thin glass membrane separating the solution of unknown pH from a solution of known concentration of H^+ ions with reference to a standard calomel electrode is first amplified and then measured with a potentiometer. The pH value is read directly from a scale.

8.14 Buffers

It is sometimes necessary that a solution of a definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If the solution comes in contact with the air, it will absorb CO_2 and become more acidic. If the solution is stored in a glass bottle, alkaline impurities leached from the glass may alter the pH.

Buffer solutions are capable of maintaining their pH at some fairly constant value even when small amounts of the acid or base are added. Thus a buffer solution is one that tends to maintain its pH when an acid or alkali is added to it. This property of such a solution is called buffer action. The capability of a buffer solution to maintain definite pH is called buffer capacity.

A buffer solution usually consists of a weakly dissociating acid and the salt of that acid with a strong base. For example.

$NaHCO_3/H_2CO_3$ and NaH_2PO_4/H_3PO_4. Suppose HCl is added to a buffer solution containing $NaHCO_3$ and H_2CO_3. The following reaction will take place.

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$

The HCl which is a strong acid and is expected to raise the pH, or $[H^+]$ reacts with a base to yield H_2CO_3 (a weak acid), and a neutral salt NaCl. The result is that provided HCl is not added in very large amounts, there would be only a little change in the original pH of the buffer solution.

In the same way if NaOH is added to this buffer solution it reacts with the H_2CO_3 as follows.

$$NaOH + H_2CO_3 \longrightarrow NaHCO_3 + H_2O$$

Since $NaHCO_3$ is a much weaker base than NaOH, the resulting rise in pH will be quite small.

A solution containing a weak base, e.g. NH_4OH and its salt with a strong acid like NH_4Cl can also act as a buffer.

Another example of buffer solution is a mixture of acetic acid, CH_3COOH and its salt with a strong base, CH_3COONa.

8.14.1 Applications of Buffers

(i) The use of buffers is an important part of many industrial processes. Examples are electroplating and the manufacture of leather, photographic materials and dyes.

(ii) The bacteriological research culture media are generally buffered to maintain a constant pH required for the growth of the bacteria being studied.

(iii) Buffers are used extensively in analytical chemistry and are used to calibrate pH.

(iv) Human blood is buffered to a pH of 7.4 by means of bicarbonates, phosphates and complex protein systems.

Example 10

A buffer solution contains 1 mol/litre each of acetic acid and sodium acetate. Find the pH.

Solution

The equation for the ionization of weak acid and its K_a can be written as

$$HA \rightleftharpoons H^+ + A^-$$

so $$K_a = \frac{[A^-][H^+]}{[HA]}$$

or $$[H^+] = \frac{[HA]}{[A^-]} \times K_a$$

The concentration of the anion A^- can be assumed to be the same as the concentration of the salt. The above expression becomes

$$[H^+] = \frac{[Acid]}{[Salt]} \times K_a$$

For the buffer containing, CH_3COOH and CH_3COON_a

$$K_a = 1.8 \times 10^{-5}$$

Thus $$[H^+] = 1.8 \times 10^{-5} \ \frac{1}{1} = 1.8 \times 10^{-5} M.$$

$$\text{or } pH = -\log(1.8 \times 10^{-5}) = -(0.26 - 5)$$

$$= 4.74$$

8.15 Indicators

Indicators are coloured organic compounds that change colour in solution as the pH of the solution changes. For example methyl orange is red in solution at pH below 3.1 and yellow in solution at pH above 4.5. The colour of this indicator is a varying mixture of yellow and red in the pH range between 3.1 and 4.5. Table 8.3 shows different indicators with different colours in acidic and alkaline media over a varied range of pH.

Indicators are weak acids or weak bases. Since they are intensely coloured, only a few drops of a dilute solution of an indicator are employed in any titration. In order to know a point at which a reaction is complete, a suitable indicator is used which changes its colour when chemically equivalent amount of the two reacting substances are present. The choice of indicator depends upon the nature of the reaction under study. There are different types of indicators.

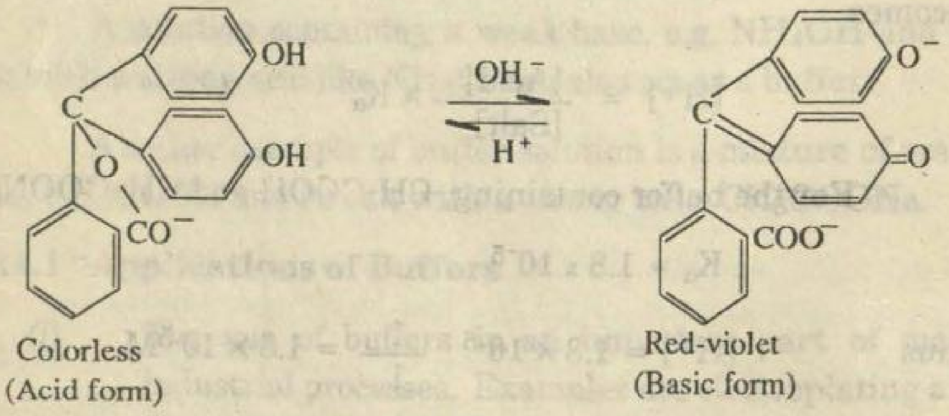
(i) Acid-base indicators

(ii) Redox indicators

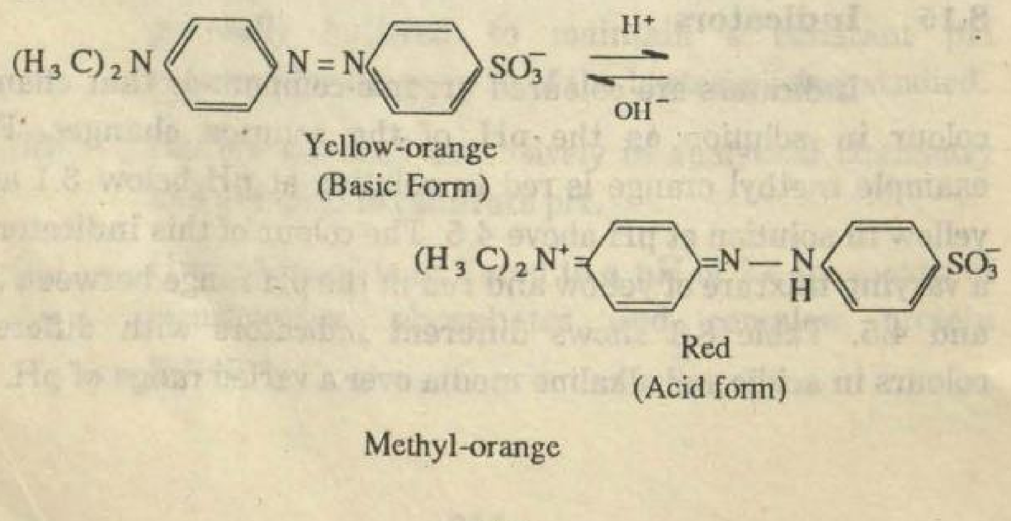
(iii) Precipitation indicators

8.15.1 Acid-base Indicators

Commonly used acid-base indicators are



Phenolphthalein



Methyl-orange

phenolphthalein and methyl orange. The former is weak acid, while the latter is weak base. The colour change of these indicators take place due to structural changes as shown.

8.15.2 Redox Indicators

Redox Indicators are dyes which undergo a reversible change on oxidation or reduction. They show different colours in the oxidized and reduced states. In Table 8.3 various redox indicators are given. Sometimes oxidizing and reducing agents may also serve as their own indicators. If the reagents are highly coloured and undergo reaction into colourless compounds, the end point will be observed by the appearance of colour when even one drop is added in excess e.g., $KMnO_4$ added to a reducing solution is converted into colourless manganous compounds until no reductant is left. One excess drop will then impart pink colour to the whole solution.

Table 8.3

Indicator	Acid	pH range of colour	Alkaline colour
Thymol blue	red	1.2--2.8	yellow
Methyl orange	red	3.1--4.5	yellow
Bromocresol green	yellow	3.8--5.5	blue
Methyl red	red	4.2--6.3	yellow
Litmus	red	5.0--8.0	blue
Bromothymol blue	yellow	6.0--7.6	blue
Thymol blue	yellow	8.0--9.6	blue
Phenolphthalein	colourless	8.3--10.0	red
Alizarin yellow	yellow	10.0--12.1	lavender

8.15.3 Precipitation Indicators

There is no suitable indicator for the precipitation reactions. However, the formation of a coloured precipitate may

indicate the end point. For example K_2CrO_4 is used as an indicator in the titration of chloride with $AgNO_3$. Ag^+ is titrated against KCNS solution. AgCNS (solid) is precipitated.

$$Ag^+ + CNS^- \longrightarrow AgCNS\ (solid)$$

At the end point a drop of potassium thiocyanate in excess may be detected from its colour change by reaction with ferric ions if present in solution. Ferric alum, therefore, is used as an indicator in this titration. Sometimes absorption indicators like fluoresceine or dichlorofluoresceine are also used for the titrations of Cl^- and Ag^+ ions.

Table 8.4

Indicator	Colour in reduced form	Colour in oxidised form	Transition emf (Volt)
Diphenylamine	colourless	Violet	−0.76
Diphenyl benzedrine	colourless	Violet	−0.76
Diphenylamine sulphonic Acid (Sodium and Barium salts)	colourless	Reddish violet	−0.84
Ferroin	red	Pale blue	−1.14
Nitroferroin	red	Pale blue	−1.25

8.16 Strength of Acids and Bases

According to Bronsted, the strength of an acid is measured from its tendency to donate a proton and that of a base from its tendency to accept a proton. Strengths are generally expressed in terms of dissociation constant Ka and pKa value of acids. Let us consider a proton acid, HX. In aqueous solution it constitutes the following equilibrium.

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

According to the law of mass action

$$K = \frac{[X^-][H_3O^+]}{[HX][H_2O]}$$

Where K is an equilibrium constant and the quantities within the square brackets denote molar concentrations or activities of the reactants and products. As water is always in excess, its concentration is constant and we have

$$\frac{[X^-][H_3O^+]}{[HX]} = K[H_2O] = K_a$$

K_a is called dissociation constant of acid and represents the extent to which an acid is dissociated. Greater the value of K_a greater will be the acid strength and vice versa. $1/K_a$ represents the strength of the base X^-. The strength of an acid can also be expressed in terms of its pK_a where

$$pK_a = \log \frac{1}{K_a} = -\log(K_a)$$

A large value of pK_a means the acid is little dissociated and a small value means that acid is highly dissociated. Thus $HClO_4$ ($Ka = 10^{10}$, $pK_a = -10.0$) is a stronger acid than HCl ($Ka = 10^7$, $pKa = -7$). For weak pKa values are high.

The strength of an acid is related to that of its conjugate base. If the acid is strong its conjugate base is weak. For example, HCl is stronger acid as it has got a great tendency to lose a proton, its conjugate base Cl^- is a weak base as it has got a little tendency to accept a proton. Reverse is true if the conjugate base is strong. The acid strength depends upon the solvent chosen. All the strong acids like $HClO_4$, H_2SO_4, HCl and HNO_3 have very close pK_a values. They appear to have nearly equal strengths in aqueous solution. This phenomenon is called levelling effect. The same effect is noticed in the case of solutions of bases. The strongest base which can exist in water is OH^- ion. The bases O^{2-} and NH_2^- are fairly strong therefore when Na_2O and $NaNH_2$ are dissolved in water, they give following reactions.

$$O^{2-}(aq) + H_2O \longrightarrow 2OH^-(aq)$$

$$NH_2^-(aq) + H_2O \longrightarrow NH_3(aq) + OH^-(aq)$$

The reactions go to completion and thus basic strength of O^{2-} and NH_2^- is levelled to the strength of OH^- ions and they behave as equally strong bases in aqueous solution. The order of decreasing Strength of stronger mineral acids has been found to be:

$$HClO_4 > HI > HBr > HCl > H_2SO_4 > HNO_3$$

The approximate values of pK_a of some of the acids are given in table 8.5

Table 8.5

Approximate pK_a Value of Some Acids

Acids	pK_a	Acids	pK_a
H_2O	16	HClO	7.2
HF	3	HBrO	8.7
HCl	−7	HIO	11.0
HBr	−9	HNO_3	−1.4
HI	−10	$HClO_3$	−1
H_2SO_4	−3	HIO_3	0.8
$HClO_4$	−10	HPO_3	−2

8.17 Hydrolysis

When a salt dissolves in water it dissociates into cations and anions. These cations and anions may react chemically with the solvent that is, H_2O. This process is called hydrolysis. For example, the cation of a salt may undergo the reaction.

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$

and the anion may react as

$$X^- + H_2O \rightleftharpoons HX + OH^-$$

Since H^+ or OH^- ions are produced in these reactions, the solution of the salt may be acidic or basic, depending upon the extent of hydrolysis reactions. Consider the following observations:

(i) Copper sulphate solution turns blue litmus red.

(ii) Sodium carbonate solution turns red litmus blue.

(iii) Sodium chloride solution has no action on litmus paper.

These observations can be explained on the basis of Bronsted - Lowry acid base theory.

The anions derived from weak acids are strong bases. For example CO_3^{2-}, HCO_3^-, S^{2-}, CN^{1-}, CH_3COO^- would react with water to produce OH^- ions which make the solution basic.

$$\underset{\text{base}}{CO_3^{2-}} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{HCO_3^-} + \underset{\text{base}}{OH^-}$$

$$\underset{\text{base}}{CH_3COO^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{OH^-}$$

The strong base CH^- makes the solution basic. Hence solutions of salts containing these ions will be basic in nature. Anions like ClO_3^-, NO_3^-, Cl^-, Br^- and I^- are so weakly basic that they would not be hydrolysed significantly.

Cations such as NH_4^+ and Cu^{2+} react with water to produce H_3O^+ ion which make the solution acidic.

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_3O^+}$$

$$\underset{\text{Acid}}{Cu^{2+}} + \underset{\text{base}}{4H_2O} \rightleftharpoons \underset{\text{base}}{Cu(OH)_2} + \underset{\text{acid}}{2H_3O^+}$$

The strong acid H_3O^+ makes the solution acidic.

The equilibrium equation for reaction of anions with water can be written as

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

and its base hydrolysis constant K_b is expressed as

$$K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

Greater the concentration of OH^- ions greater will be the K_b value and greater the basic characteristics of A^-.

Similarly the equilibrium equation of acid cations can be written as

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$$

and its acid ionization constant or acid hydrolysis constant is expressed as in which H^+ has been substituted for H_3O^+. Greater the concentration of H^+ at equilibrium stage, greater will be the K_a value. Generally speaking.

$$K_a = \frac{[H^+]\,[B]}{[BH^+]}$$

(i) Salts of strong acids and strong bases (such as NaCl) are neutral (pH = 7).

(ii) Salts of weak acids and strong bases (such as CH_3COONa) hydrolyse producing a basic solution (pH > 7).

(iii) Salts of strong acids and weak bases (such as NH_4Cl) hydrolyse producing an acidic solution (pH < 7).

(iv) Salts of weak acids and weak bases (such as CH_3COONH_4) hydrolyse, but whether the resulting solution is neutral, acidic or basic depends upon the relative values of K_a and K_b (i.e. hydrolysis constants of acid or base respectively).

EXERCISE

1. Define molarity and molality. Explain each unit with at least two examples.

2. Determine the weight of solute required to prepare each of the following solutions:-

   (a) 2 litres of 0.3M ethanol (C_2H_6O) solution Ans: (27.6g)

   (b) 2.5 litres of 1.5M NaOH solution Ans: (150g)

   (c) 400 ml of 0.85M HCl solution Ans: (12.41g)

3. Calculate the molarity of solution containing:-

   (a) 3g H_2SO_4 in 250mL of solution Ans: (0.122M)

   (b) 400g of KCl in 2 litres of solution Ans: (2.7M)

   (c) 103g of $(NH_4)_2SO_4$ in 600 mL of solution Ans: (1.32M)

   (d) 0.22g of $CuSO_4.5H_2O$ in 50mL of solution Ans: (0.0176M)

4. The concentration of Ag^+ ion is 1×10^{-6} moles/L in AgBr solution. Find the minimum concentration of Br^- ions necessary to cause precipitation of AgBr. The $Ksp = 4 \times 10^{-13}$

5. How do you differentiate between hydration and hydrolysis? Explain by giving suitable examples.

6. (a) Define and explain electrolytic conductance of solutions of electrolytes with special reference to aqueous solution of NaCl.

   (b) What is the change in the products by electrolysis of molten NaCl?

7. Explain the following terms:

   (a) Electrolytic cell

(b) Galvanic cell

(c) Half cell

(d) E.M.F. of a cell

(e) Electrode potential

(f) Daniel cell

(g) Salt bridge

(i) Standard hydrogen electrode

8. (a) What are electrochemical series. Give its applications.

(b) How does the cell reaction develops the cell voltage.

Give at least three examples by using electrochemical series.

9. Define oxidation potential of an electrode. How is it measured experimentally?

10. Given the following cells at 25°C

Zn, Zn^{2+} (1M) || (1M); I_2/Pt.

$Sn; Sn^{2+}$ (1M) || Fe^{2+} (1M); Fe.

P_t/H_2 (1 atm); H^+ (1M) || Cu^{2+}; (1M) Cu.

(a) Write the cell reactions.

(b) Calculate the voltage of each cell as written by consulting the table.

11. Define the oxidation number of an element. Calculate the oxidation number of each element in the following:

H_2SO_4, HNO_3, $K_2Cr_2O_7$, H_2CrO_4, Na_3PO_4, $NaHCO_3$, NH_4^+, $KMnO_4$, K_2MnO_4, $Cr_2(SO_4)_3$, $Ca(ClO_3)_2$

12. With the help of oxidation number method, balance the following equations:-

(a) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

(b) $KI + NaBr + H_2O \longrightarrow KOH + NaBrO_3 + I_2$

(c) $H_2S + FeCl_3 \longrightarrow S + FeCl_2 + HCl$

(d) $KClO_3 \longrightarrow KCl + O_2$

(e) $HNO_2 + HI \longrightarrow NO + I_2 + H_2O$

(f) $NnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(g) $Br_2 + NaOH \longrightarrow NaBrO_3 + NaBr + H_2O$

13. Predict which of the following reactions tend to take place spontaneously.

(a) $MgCl_2 + Zn \longrightarrow ZnCl_2 + Mg$

(b) $H_2 + 2AgNO_3 \longrightarrow 2HNO_3 + 2Ag$

14. Balance the following equations by the ion electron method:-

(a) $Sn^{2+} + Fe^{3+} \longrightarrow Sn^{4+} + Fe^{3+}$

(b) $Cr(OH)3 + H_2O_2 \longrightarrow CrO_4^{2-} + H_2O$

(c) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{2+} + NO_3^- + H_2O$

(d) $H_2O_2 + MnO_4^- + H^+ \longrightarrow Mn^{2+} + O_2 + H_2O$

(e) $Sn^{2+} + Hg^{2+} \longrightarrow Sn^{4+} + Hg$

(f) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$

(g) $Zn + Cr_2O_7^{2-} + H^+ \longrightarrow Zn^{2+} + Cr^{3+} + H_2O$

(h) $BrO_3 + I^- + H^+ \longrightarrow Br^- + I_2 + H_2O$

(i) $Sn^{2+} + I_2 \longrightarrow Sn + I^-$

15. Fill in the blanks with suitable words given in the brackets:-

(i) ______________ solution has one mole of solute in 1000 ml of solution. (molal/molar).

(ii) Number of solute particles in 100 ml of one molar NaCl are approximately ____________ to those of 100 ml of molar solution of glucose (equal/twice).

(iii) Copper sulphate is ____________ hydrated(penta/tetra)

(iv) We report the solubility products of ____________ solute salts (highly/spraingly)

(v) Solubility product ____________ the quantitative limit of solubility of the salt (gives/ does not give)

(vi) In the electrolysis of molten NaCl, __________ is collected at cathode but for aqueous solution of NaCl, __________ is collected (H_2 gas/Na-metal)

(vii) Oxidation takes place at __________ and reduction at __________ in galvanic cell (anode/cathode)

(viii) The sum of oxidation number for a neutral compound is always __________ (positive/ negative/zero)

(xi) Acidic solution has a pH __________ than 7 but a basic solution has a pH __________ than 7. (more/less)

(x) The pH of the human blood is ____________ (7.4/ 8.4)

(xi) The buffer solution of pH 4.76 is prepared by mixing __________ quantities of CH_3COOH & CH_3COONa (different/equal).

(xii) Phenolphthaline and methyl orange are ______________ indicators. (redox/acid-base).

(xiii) __________ the pKa value stronger the acid and ____________ the Ka value weaker the acid. (greater/less)

(xiv) Aqueous solution of NH_4Cl is ______ while that of $NaHCO_3$ is ______ (basic/acidic)

(xv) The sum of pH and pOH of an aqueous solution is ______ 14. (less than/equal to)

(xvi) The product of $[H^+]$ and $[OH^-]$ for pure water is -14 at ______ (25°C/all temperatures).

Q.16. Explain the followings giving reasons:

(i) Number of molecules of glucose in 1 molar and one molal aqueous solutions are equal but number of water molecules are different.

(ii) One molal solution of NaCl in water is dilute as compared to one molar solution of it.

(iii) In electrolysis of molten NaCl equal number of atoms of Na and chlorine are deposited at respective electrodes but two chlorine atoms are discharged for one Ca-atom in molten $CaCl_2$.

(iv) H_2 gas is collected at the cathode rather than sodium metal, when dilute aqueous solution of NaCl is electrolysed.

(v) Chemical energy is converted into electrical energy in Galvanic cells.

(vi) Oxidation and reduction reactions go side by side in Daniel cell.

(vii) A metal rod should be dipped in the solution of its own ions in voltanic cell.

(viii) Zn rod acts as cathode in Daniel cell but will act as anode if it is connected to Al rod dipped in the solution of $AlCl_3$.

(ix) Buffer solutions resist the change of pH, but every buffer has its own buffer capacity.

Phenolphthalein

(x) Phenolphthaline is colourless in acidic medium but pink in basic medium.

(xi) Methyl orange is yellowish orange in basic media but red in acidic media.

(xii) $KMnO_4$ itself acts as an indicator in redox titration.

(xiii) A strong acid has a weak conjugate base, while a strong base has a weak conjugate acid.

(xiv) $CuSO_4$, $AlCl_3$ and NH_4Cl give acidic aqueous solution, but Na_2CO_3 gives basic aqueous solution.

9

INTRODUCTION TO CHEMICAL KINETICS

9.1 Introduction

A chemical reaction can be described by a chemical equation but it says nothing about, how fast the reaction will take place. Among several possible reactions, all with similar negative values of ΔH, one may take place instantaneously, another may proceed slowly with measurable rate and still another may not proceed even after years. For example, the following reaction is highly spontaneous.

$$H_{2(g)} + O_{2(g)} \xrightarrow{\text{spark}} H_2O_{(l)}$$

Yet if we mix H_2 and O_2 we would have to wait for a long time, perhaps more than our life time for the completion of this reaction. On the other hand an electric spark can complete

the reaction with explosive violence. But this information is provided neither by the balanced chemical equation nor by the enthalpy change. For such additional information we must look to the field of chemical kinetics which helps us to understand what happens in between the time when reactants are undergoing a change, which results in the formation of the products.

The branch of chemistry which deals with the study of the reaction rates is known as chemical kinetics. This study tells us what happens to reactants, how molecular collisions leads to the formation of products, how bonds break and new bonds form, how a net reaction is the result of a sequence of many steps.

Several factors influence the rates of chemical reactions. These are the nature of reactants, concentration of reactants, the temperature and the presence of catalysts. The effects of these factors on the rate of a chemical reaction can provide clues to the nature of intermediate steps i.e. the mode and mechanism by which reactants are converted into products. Such a knowledge can lead us to suggest not only other possible routes of reactions but also to improve the conditions by which yield of a chemical reaction can be improved.

9.2 Reaction Rate

The rate or velocity of a chemical reaction is the change in the concentration of reactants or products in a unit time.

$$\text{Rate} = \frac{\text{change in concentration}}{\text{time period of change}} = \frac{\Delta c}{\Delta t} \qquad \text{........ (9.1)}$$

The concentrations of reactants decrease with time and the concentrations of products increase with time (Fig: 9.1). The rate of reaction may therefore be defined as the rate of decrease in the concentration of a reactant, or the rate of increase in the concentration of a product. The concentrations are expressed in the units of moles per litre and time is expressed in seconds. The reaction rate is expressed in units of moles per litre per second

(mol L^{-1} S^{-1}). The reaction rates of gases are sometimes expressed in units of partial pressure change per unit time.

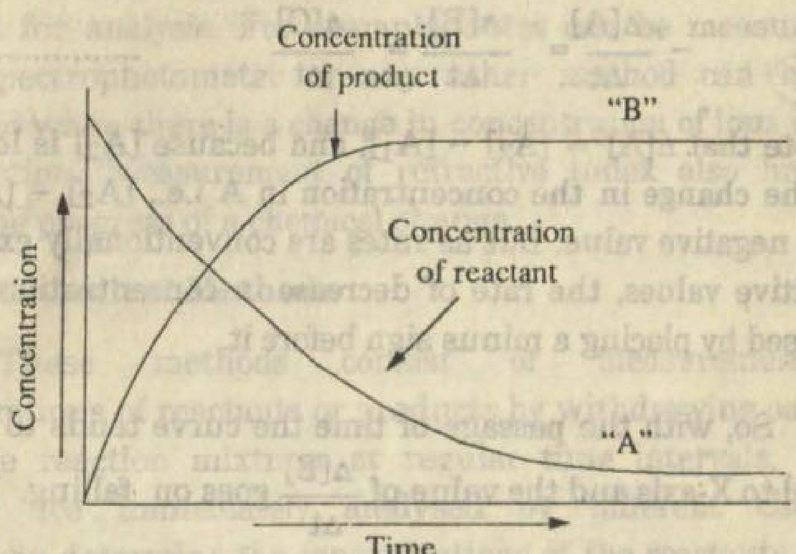


Fig. 9.1 — Change in the concentration of reactants and products with time for the reaction A ⟶ B

Consider the general reaction

$$A \longrightarrow B + C$$

Let us express the concentration of A at time t_1 as $[A_1]$ and the concentration at time t_2 as $[A_2]$. As usual, the brackets mean the concentration in moles per liter. The average rate of decrease in the concentration can be expressed as

$$\text{Average rate of decrease in A} = \frac{[A_2]-[A_1]}{t_2-t_1} = \frac{-\Delta[A]}{\Delta t}$$

The average rate of increase in B, can similarly be expressed as

$$\text{Average rate of increase in B} = \frac{[B_2]-[B_1]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

and

$$\text{Average rate of increase in C} = \frac{[C_2]-[C_1]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

where subscripts 1 and 2 denote the initial and final concentrations. As the decrease in the concentration of A is equal to the increase in concentration of B and C, we have

$$-\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \quad \text{..................} (9.2)$$

But note that $\Delta[A] = [A_2] - [A_1]$, and because $[A_2]$ is less than $[A_1]$, the change in the concentration in A i.e., $[A_2] - [A_1]$ will have a negative value. But as rates are conventionally expressed as positive values, the rate of decrease in concentration of A is expressed by placing a minus sign before it.

So, with the passage of time the curve tends to become parallel to X-axis and the value of $\frac{\Delta[B]}{\Delta t}$ goes on falling. We can have as many instantaneous rates as possible by drawing tagents at various points of this curve.

The notation (delta) shows a small change. In order to express the instantaneous $\frac{\Delta[B]}{\Delta t}$ rate of a reaction, we better express it as $\frac{d[B]}{dt}$ rather than $\frac{\Delta[B]}{\Delta t}$. If the concentration of products is denoted by 'x', the rate of reaction is expressed as $\frac{dx}{dt}$.

This $\frac{dx}{dt}$ (differential of x with respect to t) is called rate of change of concentration of products with respect to time. Here dx and dt are infinitesimally small changes in concentration and time.

9.3 Determination of Reaction Rates

Different experimental techniques are employed to measure the rate of a chemical reaction. These techniques are of two types.

(*i*) Physical methods

(*ii*) Chemical methods

(i) Physical Methods

A method which does not require the removal of successive samples from the reaction mixture is considered to be the best for analysis. For example, rates can be measured by using spectrophotometer or any other method can can be employed when there is a change in concentration of ions during the reaction. Measurement of refractive index also helps to follow the progress of a chemical change.

(ii) Chemical Methods

These methods consist of measurement of concentrations of reactants or products by withdrawing samples from the reaction mixtures at regular time intervals. These samples are immediately analysed by different chemcial methods to determine the concentrations of the reactants or the products.

One of the most common method is to measure the concentration of reactants or products volumetrically. For example, in the hydrolysis of ethyl acetate, $CH_3COO\ C_2H_5$ in the presence of an acid the reaction is followed by withdrawing samples of solution at regular intervals and the amount of CH_3COOH produced at different time intervals is noted. The different concentrations are then plotted against the time. The slope of the curve at any point on the curve can be found by drawing the tangent to the curve at time t. The rate will be equal to the slope.

9.4 Order of a Chemical Reaction

In a balanced chemical equation, certain number of atoms, molecules or ions react to give products. The number of atoms or molecules whose concentrations determine the rate of the reaction is called order of reaction.

Let us consider the reaction.

$$mA + nB \longrightarrow \text{Products}$$

The rate of reaction can be expressed as,

$$\frac{dx}{dt} = k\,[A]^x\,[B]^y$$

The k is velocity or rate constant, *m* and *n* are generally simple integers and are coefficients in balanced equation. In the rate expression the exponents may be *m* and *n* or some other integers as *x* or *y*. *x* is the order of reaction with respect to A and y is order of reaction with respect to B and *x* + *y* is called the overall order of reaction. So, we reach the conclusion that ordinarily sum of exponents in the rate expressions of a reaction is called order of reaction. Some important reactions alongwith their orders are:

(*i*) $N_2O_5 \longrightarrow 2\,NO_2 + \frac{1}{2}O_2$

$$\frac{dx}{dt} = k\,[N_2O_5] \quad \text{......................(first order reaction)}$$

(*ii*) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

$$\frac{dx}{dt} = k\,[SO_2Cl_2] \quad \text{..................(first order reaction)}$$

(*iii*) $H_2 + I_2 \rightleftharpoons 2HI$

$$\frac{dx}{dt} = k\,[H_2][I_2] \quad \text{.............(second order reaction)}$$

9.5 Rate Constants (Specific rate Constant)

The experimental relationship between a reaction rate and the concentration of the reactants is known as the rate law or the rate equation for that reaction.

$$aA + bB \longrightarrow \text{Products}$$

$$\text{Rate of reaction} = \frac{-\Delta[A]}{t} = k\,[A]^m\,[B]^n$$

where *k* is known as the rate constant or velocity constant of a reaction, *m* may be equal to *a*, and *n* to *b*, but there is no general relationship between the stoichiometric equation for a reaction and the rate expression. Indeed, *m* or *n* may be either whole

number or fractions or zero. If concentration of A and B are kept unity, then the rate of reaction is,

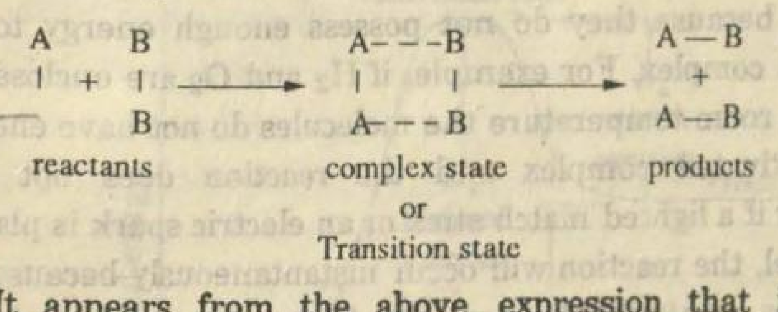
$$\frac{dx}{dt} = k\,[1]^m\,[1]^n = k$$

So, rate constant k of a reaction is nothing but rate of reaction, where concentration of reactants are unity. The rate is ever changing parameter, but rate constant is a fixed value for the reaction under given conditions of pressure, temperature, solvent etc.

9.6 Energy of Activation and the Activated Complex

A basic idea underlying all reaction mechanisms is derived from the postulates of the kinetic theory. Molecules undergo constant and random motion as a result of which they experience frequent collisions. Collision theory of reaction rates proposes that chemical reactions occur as a result of collisions between molecules. A useful extension of the collision theory is the theory of the transition state. It has been suggested that if two molecules are to react chemically, they must be in a transition state or activated complex. This is the state that exists at the instant of a potentially efficient collision. This activated complex then dissociates into products.

For example:



It appears from the above expression that if two molecules with sufficient energy collide to form this activated complex, then this collision would result in a chemical reaction. Thus only an effective molecular collision can result in the formation of a product. A possible picture of collision can be imagined as shown in (Fig. 9.2).

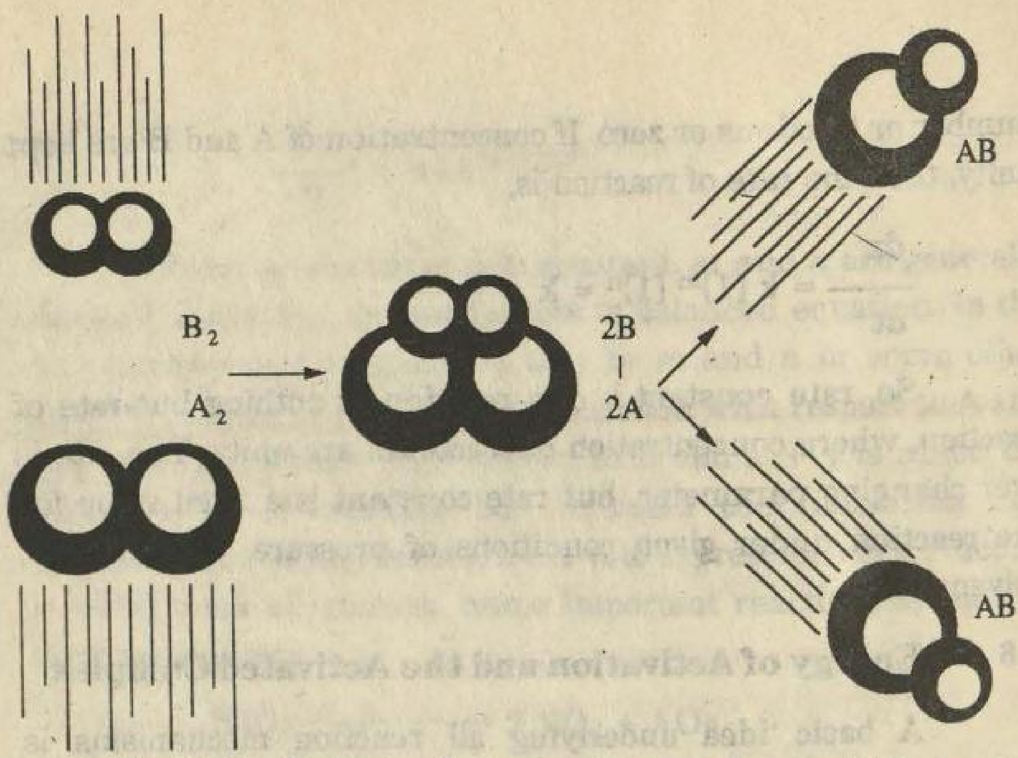


Fig. 9.2 — Mechanism for the reaction $A_2 + B_2 \longrightarrow 2AB$

For a given reaction system, the minimum amount of energy which molecules must have to form an activated complex is called the activation energy. In many reaction systems at room temperature, the value of this activation energy is much greater than the average kinetic energy of the molecules. The reaction therefore does not take place. But if some molecules acquire energies more than the average kinetic energy then these molecules do react, when they collide with each other while moving in a random way. However, for many exothermic reactions the molecules simply rebound after collisions without reacting because they do not possess enough energy to form activated complex. For example, if H_2 and O_2 are enclosed in a vessel at room temperature the molecules do not have energy to form activated complex and the reaction does not occur. However if a lighted match stick or an electric spark is placed in the vessel, the reaction will occur instantaneously because some molecules gain enough energy to form activated complex and start the reaction. Once the reaction starts the heat released by activated complexes provides energy to the remaining molecules to complete the reaction. On the other side, if the temperature is decreased, there is a decrease in number of effective collisions to form activated complex and hence the rate of reaction decreases

with lowering of temperature. From this discussion we can say that, the velocity of a molecular chemical reaction is an indication of the number of molecules that become activated per unit time.

The energy of activation is usually expressed in joules and kilo joules and is denoted by the symbol E_a. The relationship between enthalpy of reaction and energy of activation for an exothermic reaction is shown in Figure 9.3(a) and the same

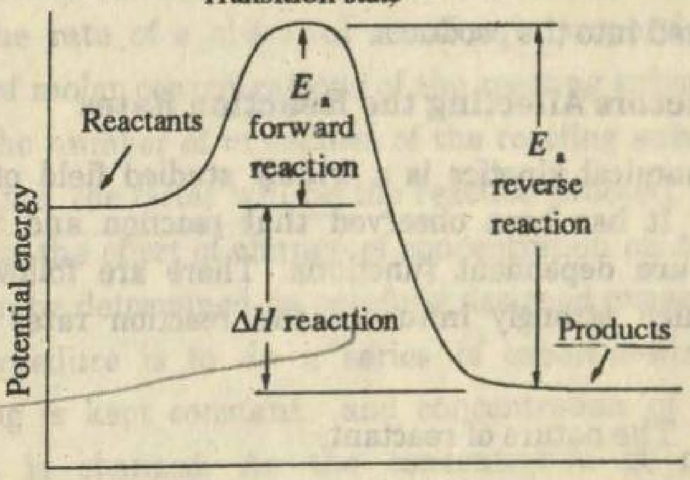


Fig. 9.3 (a) Activation energy and heat of reaction of exothermic reaction.
(ΔH = Net energy released)

relationship is shown for an endothermic reaction in Fig. 9.3(b).

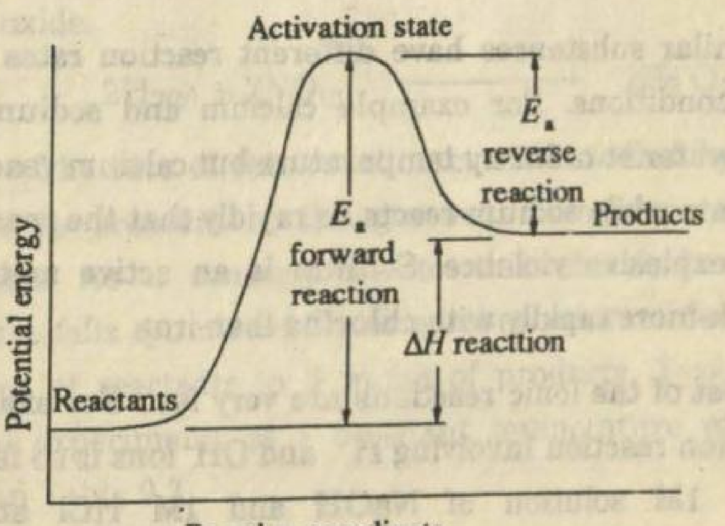


Fig. 9.3 (b) Activation energy and heat of reaction of endothermic reaction.
(ΔH = Net energy obserbed

In an exothermic reaction products are at a lower energy level than the reactants and in an endothermic process the products are at a higher energy level than the reactants. With both types of reactions the activation energy is an *energy barrier* which must be overcome before products can be formed. Surmounting this barrier is similar to carrying a ball to the top of a hill and then rolling down the either side. But if the ball can not be carried to the top, it will role back. Similarly if E_a is not supplied, the reaction will not start and the reactants will never get converted into the products.

roll

9.7 Factors Affecting the Reaction Rates

Chemical kinetics is a widely studied field of physical chemistry. It has been observed that reaction and their rate constants are dependent functions. There are following four factors which strongly influence the reaction rates and rate constants.

(*i*) The nature of reactant.

(*ii*) The concentration of reactants.

(*iii*) The temperature of the system.

(*iv*) The presence of a catalyst.

9.7.1 Nature of the Reactants

Similar substances have different reaction rates under the same conditions. For example calcium and sodium both react with water at ordinary temperature but calcium reacts at a moderate rate while sodium reacts so rapidly that the reaction is almost of explosive violence. Sodium is an active metal and reacts much more rapidly with chlorine than iron.

Most of the ionic reactions are very fast. For example a neutralization reaction involving H^+ and OH^- ions is so fast that mixing of 1M solution of NaOH and 1M HCl at room

temperature would complete the reaction in less than 10^{-6} sec. Molecular reactions have usually moderate speed.

So, the rates of reactions are highly dependent upon the nature of reactants.

9.7.2 The Effect of Concentration

Law of mass action can explain the effect of change of concentration upon reaction rate. According to law of mass action, the rate of a chemical reaction is proportional to the product of molar concentrations of the reacting substances. The greater the number of molecules of the reacting substances per unit volume, the faster will be the reaction proceed. In order to investigate the effect of change of concentration on the reaction rate it can be determined by carefully designed experiment. The usual procedure is to do a series of experiments in which everything is kept constant and concentration of one of the reactants is changed. As the concentration of one of the reactants is systematically changed, the reaction rate of each change is measured by noting the disappearance of a reactant or appearance of a product.

Let us consider the reaction between hydrogen and nitric oxide.

$$2H_{2(g)} + 2NO_{(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

The rate of this reaction can be studied by noting the change in pressure of the gaseous mixture as the reaction proceeds. As a consequence to this chemical change, gas pressure falls symmetrically as gaseous mixture decreases from 4 moles of reactants to 3 moles of products. Typical data for several experiments at a constant temperature of 800°C are given in Table 9.2.

Table 9.2

Experiment	Initial molar concentration. [NO]	[H_2]	Initial rate atm/min
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.025
6	0.003	0.009	0.056

It is noticed that in the first three experiments the initial concentration of NO is the same but differ in initial concentration of H_2; while the last three experiments have the same initial concentrations of H_2, but differ in initial concentrations of NO.

Experiments 1 and 2 show that when the initial concentration of NO is kept constant at 0.006 M, doubling the concentration of H_2 from 0.001 M to 0.002 M, doubles the rate from 0.025 to 0.050 atm/min. Similarly experiments 1 and 3 show that tripling the concentration of H_2 triples the rate. The rate of reaction is therefore, proportional to the first power of concentration of H_2. Experiments 4 and 5 show that when initial concentration of H_2 is kept constant, doubling the concentration of NO raises the rate to 4 times and experiments 4 and 6 show that tripling the concentration of NO makes the rate nine times $(3)^2$. The rate of reaction is therefore, proportional to the square of the concentration of NO. The data can be summarised by stating that the reaction rate is proportional to

$$(\text{concentration of } H_2) \times (\text{concentration of NO})^2$$

$$\text{Rate} = k\,[H_2]\,[NO]^2$$

The equation is known as the rate law for the reaction. It is evident that such rate law cannot be predicted from the balanced chemical equation.

9.7.3 Effect of Temperature

Raising the temperature generally increases the rate of any chemical reaction whether the reaction is an endothermic or an exothermic one. The change of rate with temperature is expressed by a change in the specific rate constant k. The magnitude of change varies with temperature and nature of the reaction. Generally a 10^0C rise in temperature approximately doubles the reaction rate. However, the effect of temperature is to be determined experimentally in each case.

Arrhenius explained the effect of temperature on rate constant of a chemical reaction. According to his mathematical relationship.

$$k = Ae^{-\frac{Ea}{RT}} \quad \text{..................................} (1)$$

Where k = rate constant

R = gas constant

A = Arrhenius constant and depends upon the nature of gas.

T = absolute temperature

e = base of natural logarithmic system.

Ea = energy of activation.

The equation indicates that increase of temperature increases k and vice versa.

Energy of activation is the minimum amount of energy in addition to the average energy which is just sufficient to convert the reactants to products.

The equation shows that (1) greater the energy of activation, lesser would be the rate constant and (2) higher the temperature, greater would be the rate constant of a reaction.

When the exponential form of equation is expressed in term of log system, it is as under.

$$\log k = \text{Log}\, A - \frac{Ea}{2.303\, RT} \quad \text{.............} \quad (2)$$

This is equation of straight line, and when a graph is plotted between log k on y- axis and $^1/_T$ on x-axis, a straight line is obtained. The slope of straight line gives the value of energy of activation.

It is clear that at a given temperature, every molecule does not posses same quantity of energy. Some of molecules are at lower energy than average ones while some are at higher energy. The idea of change of reaction rate with possession of energy is understood from a graph. The distribution of molecular kinetic energies is shown in the following figure for two temperatures where $T_2 > T_1$. The curve at any temperature shows that a certain fraction of molecules have a definite energy range. If minimum energy required for reaction to take place is Ea, then number of molecules possessing at least this energy at each temperature is given by the area of the shaded region under each curve (Fig: 9.4).

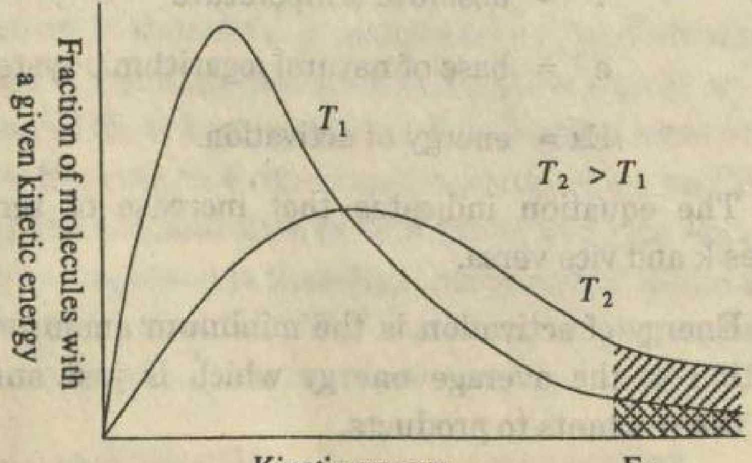


Fig. 9.4 At higher temperatures the fraction of molecules above the Ea is much greater.

The diagram indicates that a small increase in kinetic energy can result in a corresponding increase of activation energy of molecule. As the number of molecules with the necessary energy increases, the rate of reaction increases proportionately.

9.8 Catalysis

A catalyst is a substance which changes the rate of a chemical reaction without itself being consumed in the process. This process is known as catalysis. The catalyst takes an active part in the reaction but suffers no chemical change and for this reason does not appear in the equation for overall reaction. For example, acid catalysed decomposition of formic acid is represented as below.

$$HCOOH \xrightarrow{(H^+)} H_2O + CO$$

Although, a catalyst can be recovered entirely at the end of chemical process, yet it is quite common that the catalyst undergoes a physical change, such as a change in crystal size, or form, or a change in degree of hydration.

9.8.1 The Types of Catalysis

Catalysis is of two types:-

(i) Homogeneous catalysis

(ii) Heterogeneous catalysis.

Homogeneous catalysis is that when the catalyst and the reactants are present in the same phase.

A heterogeneous catalyst exists in the separate phase from the reactant and can be recovered by filteration.

To understand the types of catalysis let us follow the formation of sulphuric acid. It is one of the most important chemicals, the production of which is vital to the economy of a country. The formation of sulphuric acid can be represented by the following simplified chemical equations.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

The critical reaction in this sequence of equations is in which SO_2 changes to SO_3. The rate of this reaction is very slow, and hence the production of H_2SO_4 is low. The reaction is slow because it has very high activation energy and does not occur to an appreciable extent at ordinary temperature. So we feel the need of a catalyst which may lower the activation energy for the reaction to take place at moderate temperature. There are two ways in which this process can be affected. In the old lead chamber process for sulphuric acid manufacture the reactants SO_2, O_2 and H_2O are mixed with NO and NO_2 and passed through the chambers. The reaction is considered to follow the path given below in which nitrosylsulphuric acid, (HSO_4. NO) is an intermediate.

$$NO + NO_2 + 2SO_2 + O_2 + H_2O \longrightarrow 2HSO_4.NO$$

The nitrosylsulphuric acid subsequently reacts with water to generate sulphuric acid.

$$2HSO_4NO + H_2O \longrightarrow 2H_2SO_4 + NO + NO_2$$

The reaction takes place at room temperature and the catalyst (NO + NO_2) is recovered at the end of reaction. This clearly indicates that the catalyst has decreased the energy of activation. This example illustrates the process of homogeneous catalysis.

A second method for this reaction is to allow the reaction on the surface of a solid catalyst V_2O_5. when it takes place with higher speed. This is done in the manufacture of sulphuric acid by the more modern contact process. The oxidation of SO_2 to SO_3 is speeded up by passing the mixture of SO_2 and O_2 over platinised asbestos or vanadium pentoxide. The resultant SO_3 is then absorbed in H_2O or H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$$

$$SO_{3(g)} + H_2SO_{4(l)} \longrightarrow H_2S_2O_{7(l)}$$

$$H_2S_2O_{7(l)} + H_2O \longrightarrow 2H_2SO_{4(aq)}$$

This is an example of heterogeneous catalysis. Heterogeneous catalysis is much more widely employed in industry than the homogeneous one. Cracking of petroleum, reforming of hydrocarbons, preparation of NH_3 etc., are carried out with the aid of solid heterogeneous catalysts. But heterogeneous catalysts are often poisoned. The impurities in the reactants coat the catalyst with unreactive material. The surface is modified and in this way catalyst activity is lost.

9.8.2 The functions of a Catalyst

The main function of a catalyst is to lower the activation energy for the process because if the activation energy is lowered, the number of molecules which possess this energy will become much larger and consequently the rate of reaction would increase. The catalysed reaction can be represented diagrammatically as in Fig. 9.5.

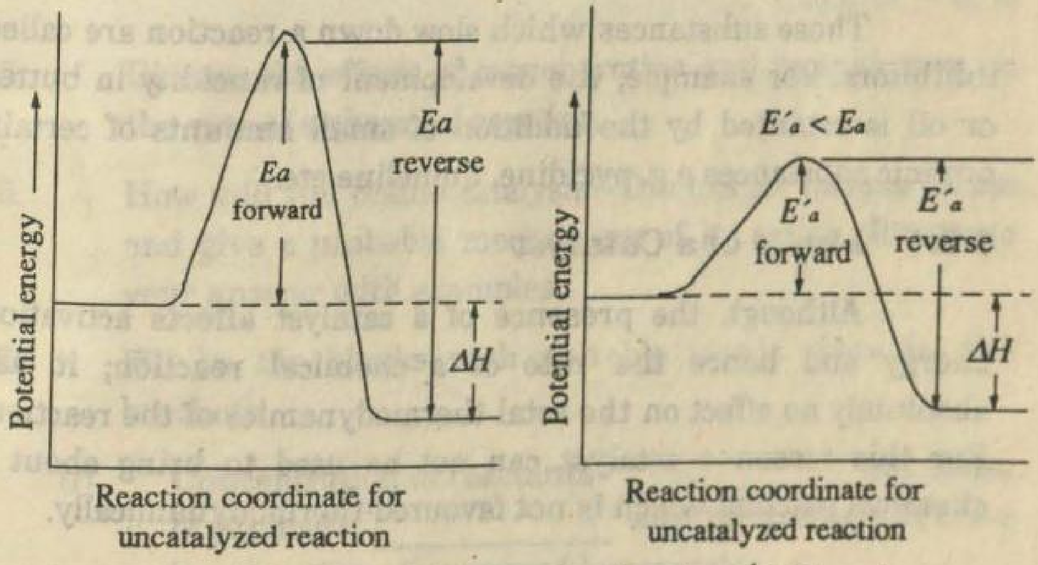


Fig. 9.5 — The function of catalyst is to lower the *Ea* value. ΔH remains the same.

As it is clear from the Figure: 9.5, *the mechanism of* catalysed reaction involves a lowering of activation energy. In case of heterogeneous catalysis, the precise mechanism is imperfectly understood. It appears that the availability of

electrons on the surface of atoms and active sites of the catalyst play the key role. For this reason the catalytic activity is associated with a large number of the transition elements and their compounds.

A catalyst is specific in nature and catalyses one reaction and may have no effect on another reaction, even if both reactions are very similar.

Those substances which make a catalyst more effective are called promoters. A small amount of a promoter may encourage the formation of lattice defects.

9.8.3 Poisoning of a Catalyst

A catalyst can be deactivated by the presence of even a small amount of impurity. This is known as a poisoning of catalyst. For example even if a small impurity of arsenic, (As), is present in Pt,it would destroy the catalytic activity of the Pt by forming platinum arsenide at the active sites on the surface of catalyst.

Those substances which slow down a reaction are called inhibitors. For example, the development of rancidity in butter or oil is retarded by the addition of small amounts of certain organic substances e.g. pyridine, quinoline etc.

9.8.4 Limits of a Catalyst

Although the presence of a catalyst affects activation energy and hence the rate of a chemical reaction; it has absolutely no effect on the total thermodynamics of the reaction. For this reason a catalyst can not be used to bring about a chemical reaction which is not favoured thermodynamically.

EXERCISE

1. Explain the meaning of the following basic terms.

   (*a*) Chemical kinetics (*b*) Collision theory

   (*c*) Activated complex.

2 Explain the following:

(*a*) Activation energy

(*b*) Rate of chemical reaction

(*c*) Rate Law

(*d*) Arrhenuis question

3. What is meant by the order of a reaction? What are the differences among first order, second order and third order reactions.

4. In the reaction A = B + 2C regardless of the order of reaction, which of the following statements are true? Give reasons:-

(*a*) Rate of disappearance of A = k[A]

(*b*) Rate of formation of B = rate of formation of C

(*c*) Rate of formation of C=2 x rate of disappearance of A

(*d*) Rate of formation of C = rate of disappearance of A.

(Answer = a, c)

5. Discuss the effects of concentration and temperature on the rate of a chemical reaction.

6. How will you define catalysis? Discuss its various forms and give a probable mechanism of its action. Illustrate your answer with examples.

7. Fill in the blanks with suitable words given in the brackets.

(*i*) Concentration of reactants ____________ but those of products ____________ with the passage of time in a reaction. (increases/decreases)

(*ii*) The time for the completion of Ist order reaction ____________ on the concentration of reactants. (depends/does not depend)

(*iii*) Instantaneous rate is expressed as __________ .

$\left(\frac{\Delta\,(conc.)}{\Delta\,(time)} \Big/ \frac{d\,(conc.)}{d\,(time)} \right)$

(*iv*) The rate of a reaction is __________ rate of change of concentration of reactants with respect to time. (-ve / +v)

(*v*) The units of first order rate constant are __________ . (sec/sec^{-1})

(*vi*) Increase of temperature __________ the rate of a chemical reaction. (increases/decreases)

(*vii*) The heat content of products is less than reactants for __________ reactions but reverse is true for __________ reactions. (endothermic/exothermic)

(*viii*) The energies of activation __________ the rate constants of a reaction. (control/do not control)

(*ix*) A catalyst changes the __________ of a reaction . (enthalpy change/energy of activation)

(*x*) A catalyst __________ start the thermodynamically unfavourable reaction. (can/cannot)

8. Explain the following with reasons:

(*a*) Energy of activation is necessary to complete a reaction.

(*b*) Increase of temperature increases the reaction rate.

(*c*) Order of reaction is not necessarily the sum of coefficients in the balanced equation.

APPENDIX-I

SI Units

Measurements of the physical sciences are based on just a few *base quantities*. These, *base units* are given in Table 1. All other quantities, called *derived quantities,* can be expressed in terms of these base quantities, and are given in Table 2. Pressure, the force per unit area, is an example of a derived *quantity*. Force, which enters into the definition of pressure, is derived quantity for which the measuring unit is the *newton*, with symbol N. The newton is the amount of force that will give a mass of one kilogram an acceleration of one meter per second per second. Thus we have the unit relation $N = kg \times (m^2 s^{-2}) = kgm^2 s^{-2}$

Table 1. Basic SI Units

Physical Quantity	Name of Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K

Table 2. Derived SI Units

Physical Quantity	SI name or Special name	SI symbol
Area	square meter	m^2
Volume	cubic meter	m^3
Density	kilogram/cubic meter	$kg\ m^{-3}$
Velocity	meter/second	$m\ s^{-1}$
Force	newton (N)	$kg\ m\ s^{-2} = J\ m^{-1}$
Pressure	newton/squar meter	$N\ m^{-2}$
Energy	joule (J)	$kg\ m^2\ s^{-2} = N\ m$
Power	watt (W)	$kg\ m^2\ s^{-3} = J\ s^{-1}$
Electric charge	coulomb (C)	A s

Table 3. Examples of Non-SI Units

Physical Quantity	Name	SI Equivalent
Length	angstrom (A°)	10^{-10} m
	inch (in)	0.0254 m
	foot (ft)	0.3048 m
Volume	liter (L)	10^{-3} m^3
Mass	pound (lb)	0.4535924 kg
Force	dyne (dyn)	10^{-5} N
Pressure	atmosphere (atm)	101,325 N m^{-2}
	torr (mmHg)	133.322 N m^{-2}
	bar	10^5 N m^{-2}
Energy	erg	10^{-7} J
	Calorie (cal)	4.1840 J
	electronvolt (eV)	0.16021×10^{-18} J
Viscosity	poise (P)	10^{-1}kg m^{-1} s^{-1}
Dipole moment	debye	3.338×10^{-30} m C

Table 4. Prefixes for Fractions and Multiples in the SI System

10^{12}	tera	T
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f

Table 5
VALUES OF PHYSICAL AND CHEMICAL CONSTANTS

Speed of light	c	$= 2.99792 \times 10^8$ m s^{-1}
Electron charge	e	$= 1.60219 \times 10^{-19}$ C
Mass of electron	m_e	$= 9.10953 \times 10^{-31}$ kg
Mass of proton	m_p	$= 1.67265 \times 10^{-27}$ kg
Mass of neutron	m_n	$= 1.67495 \times 10^{-27}$ kg
Planck constant	h	$= 6.62618 \times 10^{-34}$ Js
Vacuum permitivity	$\in_o$	$= 8.85419 \times 10^{-12}$ C^2 N^{-1} m^{-2}
Bohr radius	a_o	$= 5.29177 \times 10^{-11}$ m = 52.9177pm
Avogadro constant	N_A	$= 6.02204 \times 10^{-23}$ mol^{-1}
Gas constant	R	$= 8.31442$ JK^{-1} mol^{-1}
		$= 0.0831442$ L bar K^{-1} mol^{-1}
Boltzman constant	k	$= \dfrac{R}{N_A} = 1{,}38066 \times 10^{-23}$ J K^{-1}
Faraday constant	F	$= eN_A = 96{,}484.6$ C mol^{-1}
Acceleration due to gravity (at 45° latitude)	g	$= 9.81$ m s^{-2}

Table 6
OFTEN-USED CONVERSION FACTORS

1L =	$10^{-3}m^3$, 1mL = 10^{-6} m^3
1 atm =	1.01325 bar (1 atm ≃ 76 cm Hg, 1 bar ≃ 75 cm Hg)
1 cal =	4.184 J
1 A° =	100 pm, 1 A° = 0.1 nm
1 amu =	1.66056×10^{-27}kg

Table 7
ENERGY CONVERSION FACTORS

	kJ mol^{-1}	kcal mol^{-1}	J $molecule^{-1}$	eV	cm^{-1}
1kJmol^{-1} =	1	0.23901	1.6605×10^{-21}	0.010363	83.591
1kcal mol^{-1} =	4.1840	1	6.9478×10^{-21}	0.043360	349.73
1J $molecule^{1}$ =	$6.02220 \times 10^{+20}$	$1.4393 \times 10^{+20}$	1	$6.2414 \times 10^{+18}$	$5.034 \times 10^{+22}$
1eV =	96.490	23.062	1.6022×10^{-19}	1	8066
1cm^{-1} =	0.011963	2.8594×10^{-3}	1.9865×10^{-23}	1.2397×10^{-4}	1

Electron volts and wave numbers (cm^{-1}) are defined as amounts of energy per particle.

APPENDIX-II

Electronic configuration (*Continued*)

Z	Atom	Orbital electronic configuration	Z	Atom	Orbital electronic configuration
1	H	$1s^1$	53	I	$(Kr)5s^24d^{10}5p^5$
2	He	$1s^2$	54	Xe	$(Kr)5s^24d^{10}5p^6$
3	Li	$(He)2s^1$	55	Cs	$(Xe)6s^1$
4	Be	$(He)2s^2$	56	Ba	$(Xe)6s^2$
5	B	$(He)2s^22p^1$	57	La	$(Xe)6s^25d^1$
6	C	$(He)2s^22p^2$	58	Ce	$(Xe)6s^24f^15d^1$
7	N	$(He)2s^22p^3$	59	Pr	$(Xe)6s^24f^3$
8	O	$(He)2s^22p^4$	60	Nd	$(Xe)6s^24f^4$
9	F	$(He)2s^22p^5$	61	Pm	$(Xe)6s^24f^5$
10	Ne	$(He)2s^22p^6$	62	Sm	$(Xe)6s^24f^6$
11	Na	$(Ne)3s^1$	63	Eu	$(Xe)6s^24f^7$
12	Mg	$(Ne)3s^2$	64	Gd	$(Xe)6s^24f^75d$
13	Al	$(Ne)3s^23p^1$	65	Tb	$(Xe)6s^24f^9$
14	Si	$(Ne)3s^23p^2$	66	Dy	$(Xe)6s^24f^{10}$
15	P	$(Ne)3s^23p^3$	67	Ho	$(Xe)6s^24f^{11}$
16	S	$(Ne)3s^23p^4$	68	Er	$(Xe)6s^24f^{12}$
17	Cl	$(Ne)3s^23p^5$	69	Tm	$(Xe)6s^24f^{13}$
18	Ar	$(Ne)3s^23p^6$	70	Yb	$(Xe)6s^24f^{14}$
19	K	$(Ar)4s^1$	71	Lu	$(Xe)6s^24f^{14}5d^1$
20	Ca	$(Ar)4s^2$	72	Hf	$(Xe)6s^24f^{14}5d^2$
21	Sc	$(Ar)4s^23d^1$	73	Ta	$(Xe)6s^24f^{14}5d^3$
22	Ti	$(Ar)4s^23d^2$	74	W	$(Xe)6s^24f^{14}5d^4$
23	V	$(Ar)4s^23d^3$	75	Re	$(Xe)6s^24f^{14}5d^5$
24	Cr	$(Ar)4s^13d^5$	76	Os	$(Xe)6s^24f^{14}5d^6$
25	Mn	$(Ar)4s^23d^5$	77	Ir	$(Xe)6s^24f^{14}5d^7$
26	Fe	$(Ar)4s^23d^6$	78	Pt	$(Xe)6s^14f^{14}5d^9$
27	Co	$(Ar)4s^23d^7$	79	Au	$(Xe)6s^14f^{14}5d^{10}$
28	Ni	$(Ar)4s^23d^8$	80	Hg	$(Xe)6s^24f^{14}5d^{10}$
29	Cu	$(Ar)4s^13d^{10}$	81	Tl	$(Xe)6s^24f^{14}5d^{10}6p^1$
30	Zn	$(Ar)4s^23d^{10}$	82	Pb	$(Xe)6s^24f^{14}5d^{10}6p^2$
31	Ga	$(Ar)4s^23d^{10}4p^1$	83	Bi	$(Xe)6s^24f^{14}5d^{10}6p^3$
32	Ge	$(Ar)4s^23d^{10}4p^2$	84	Po	$(Xe)6s^24f^{14}5d^{10}6p^4$
33	As	$(Ar)4s^23d^{10}4p^3$	85	At	$(Xe)6s^24f^{14}5d^{10}6p^5$
34	Se	$(Ar)4s^23d^{10}4p^4$	86	Rn	$(Xe)6s^24f^{14}5d^{10}6p^6$
35	Br	$(Ar)4s^23d^{10}4p^5$	87	Fr	$(Rn)7s^1$
36	Kr	$(Ar)4s^23d^{10}4p^6$	88	Ra	$(Rn)7s^2$
37	Rb	$(Kr)5s^1$	89	Ac	$(Rn)7s^26d^1$
38	Sr	$(Kr)5s^2$	90	Th	$(Rn)7s^26d^2$
39	Y	$(Kr)5s^24d^1$	91	Pa	$(Rn)7s^25f^26d^1$
40	Zr	$(Kr)5s^24d^2$	92	U	$(Rn)7s^25f^36d^1$
41	Nb	$(Kr)5s^14d^4$	93	Np	$(Rn)7s^25f^46d^1$
42	Mo	$(Kr)5s^14d^5$	94	Pu	$(Rn)7s^25f^6$
43	Tc	$(Kr)5s^24d^5$	95	Am	$(Rn)7s^25f^7$
44	Ru	$(Kr)5s^14d^7$	96	Cm	$(Rn)7s^25f^76d^1$
45	Rh	$(Kr)5s^14d^8$	97	Bk	$(Rn)7s^25f^9$
46	Pd	$(Kr)4d^{10}$	98	Cf	$(Rn)7s^25f^{10}$
47	Ag	$(Kr)5s^14d^{10}$	99	Es	$(Rn)7s^25f^{11}$
48	Cd	$(Kr)5s^24d^{10}$	100	Fm	$(Rn)7s^25f^{12}$
49	In	$(Kr)5s^24d^{10}5p^1$	101	Md	$(Rn)7s^25f^{13}$
50	Sn	$(Kr)5s^24d^{10}5p^2$	102	No	$(Rn)7s^25f^{14}$
51	Sb	$(Kr)5s^24d^{10}5p^3$	103	Lr	$(Rn)7s^25f^{14}6d^1$
52	Te	$(Kr)5s^24d^{10}5p^4$			

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